1-2009

Extraction of Hydrocarbons and Minimizing Organic Deposits from Crude Oil Using Carbon Dioxide

Adel Adib Azzam

United Arab Emirates University
Deanship of Graduate Studies
M.Sc. Program in Environmental Science

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By

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A thesis submitted to the

United Arab Emirates University

In partial fulfillment of the requirements

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2008/2009

DEDICATION

I dedicate my efforts in this thesis to my parents: ***Adib Azzam & Najat Azzam,*** *brothers:* ***Rami & Hadi*** *and to my best friend* ***Iman Abu Ghali*** *for their love, care, continuous encouragement and extraordinary support throughout these years.*

ACKNOWLEDGMENTS

By God's will and grace, the present work is accomplished. All the praise and thanks are due to him. Many people have contributed to this thesis in many different ways, to a smaller or larger extent, and I am very thankful to all of them.

A special acknowledgement is to H.H. Sheikh ABDULLAH BIN ZAYED AL NAHYAN for supporting me to get enrolled in the master program at the UAE University; whom without his support I would never have achieved this endeavor.

I would like to express my sincere gratitude to my supervisor, Dr. Ali H. Al-Marzouqi, Associate Professor in the Chemical and Petroleum Engineering Department at UAE University for giving me the opportunity to work and learn from his expertise in the area of supercritical fluid extraction. His advice, discussions and personal and professional support are greatly appreciated. I will keep him always as a good example of success.

Finally, I deeply thank Dr. Taoufik Zoubeidi, Associate Professor in the Statistics Department, Prof. Abdulrazag Y. Zekri, Professor in the Chemical & Petroleum Engineering Department, and Mr. Stewart Johan Brooker, English Lecturer at UAE University for their assistance during execution of this work. Also, I do appreciate the help of my colleagues at the Chemical and Petroleum Engineering Department of UAE University, where most of the experimental work was carried out, and to every one who contributed somehow to this work.

Thank you all.

ABSTRACT

Supercritical fluid extraction (SFE) technology is a new and powerful separation process, which has several applications in environmental and petroleum industry fields. Supercritical carbon dioxide (SC CO_2) extraction process can be applied as a remediation technique for sediments contaminated with crude oil. On the other hand, SC CO_2 can be applied as an Enhanced Oil Recovery (EOR) technique in the petroleum industry to increase the ultimate recovery factor of crude oil from reservoirs. Therefore, utilization of SC CO_2 for the extraction applications can result both in environmental and economical benefits.

In this study, SC CO_2 was used for the extraction of petroleum hydrocarbons from sediments partly saturated with crude oil from Bu Hasa oil field of UAE. The effect of CO_2 flow rate (1 and 4 ml/min), temperature (80 and 160 °C), pressure (250 and 350 bar) and addition of 5% (v/v) organic solvent (heptane or toluene) in the SC CO_2 extraction was investigated. The highest extraction of hydrocarbons (up to 92 %) was obtained at 80 °C and 350 bar using modified SC CO_2 with 5% (v/v) heptane. The residual hydrocarbon profile for the sediment, after the extraction process, shows that SC CO_2 is an excellent remediation technique, where up to 93 % of Total Petroleum Hydrocarbon (TPH) in the contaminated sediment was removed. In addition, a significant reduction in levels of some Polycyclic Aromatic Hydrocarbons (PAHs) was observed. Moreover, the SC CO_2 extraction of petroleum hydrocarbons from sediment and limestone particles spiked with crude oil was conducted at the reservoir conditions (300 bar, 120 °C).

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ACRONYMS

Abbreviation	Meaning
CO_2	Carbon Dioxide
SC CO_2	Supercritical Carbon Dioxide
SCF	Supercritical Fluid
SFE	Supercritical Fluid Extraction
EOR	Enhanced Oil Recovery
TPH	Total Petroleum Hydrocarbons
PAHs	Polycyclic Aromatic Hydrocarbons
PCBs	Polychlorinated Biphenyls
SEM	Scanning Electron Microscopy
CLU	Central Laboratory Unit
ANOVA	Analysis of variance
LOD	Limit of detection

CONVERSION TABLE

Pressure Units

1 bar = 0.987 atm = 14.504 psi = 0.1 MPa

Temperature Units

$$T\,(K) = T(°C) + 273.15$$

$$T\,(°C) = 5/9 \times (T(°F) - 32)$$

Viscosity Units

Centipoise: 1 cP = 0.001 Pa·s = 1 mPa·s

CHAPTER 1

REMEDIATION BY SUPERCRITICAL CARBON DIOXIDE

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REMEDIATION BY SUPERCRITICAL CARBON DIOXIDE

1.1. Introduction

Many places of the world, i.e. industrial areas, are contaminated by a number of pollutants, either through a continuous process of contamination that might have taken place throughout many years, or by a sudden dispersion caused by an accident, i.e. oil spilling from a gas station due to a pipe breakage. The contaminants that can be found in soils are many: inorganic, like heavy metals, as well as organic, such as Polycyclic aromatic hydrocarbons (PAHs).[1,2] Soil contamination by petroleum products causes significant concern. This concern raises primarily from health risks, both of direct contact and from contamination of surface and ground water supplies.[3]

Petroleum, like all fossil fuels, mainly consists of a complex mixture of molecules called hydrocarbons. The hydrocarbon molecules that make up crude oil and petroleum products include hazardous complex chemical mixtures, such as total petroleum hydrocarbons (TPH), polycyclic aromatic hydrocarbons (PAHs) and heavy metals. Therefore, contamination of soil by petroleum hydrocarbons in large concentrations can be hazardous to the health of plants, animals, and humans.[4,5] The impact of petroleum pollution can be large, and is usually highly unpredictable. The Exxon Valdez oil spill, for example, in March 1989, was reported to affect 1750 km of the Alaskan shoreline and killed more than 30,000 seabirds.[6]

Government, industry, and the public now recognize the potential dangers that petroleum hydrocarbon compounds pose to human health and the environment. Contaminated soils can reduce the usability of land for development; and weathered petroleum residuals may stay bound to soils for years resulting in a long-term persistent

source of contamination to soil and water supplies, i.e. groundwater, at many sites around the world.[7] Therefore, petroleum hydrocarbon pollution is a pervasive, global problem; and the removal/extraction of hydrocarbon compounds from contaminated soil is an important and challenging problem.

Remediation of contaminated soils by a plethora of chemicals at wide levels of contamination can be carried out according to a number of methods. The most important and widely used remedial technologies are incineration, thermal desorption, bioremediation, chemical treatment and solvent extraction (which includes supercritical fluid extraction).[8,9] Some of them are in situ applications, other require ex situ applications where the soil/sediment are excavated/dredged [10-12]. Conventional techniques such as landfill disposal, thermal desorption, incineration and liquid solvent extraction are expensive and involve risks associated with air and residual pollution [13,14]. Biological remediation is a rather slow process, with possible logistic and practical disadvantages.[15]

Despite great efforts and expenditure of resources to develop both technically and economically effective cleanup processes of contaminated sediments, no widely accepted methods have been found and further research is still needed. New methods are therefore being investigated in order to improve the remediation efficiency and lower the costs or the remediation time. Supercritical Fluid Extraction (SFE) is one of the new methods for the remediation of hydrocarbon-contaminated sediment.[16] There is general agreement in recognizing SFE as a rather efficient, fast and clean treatment for sediment remediation.[17] The unique properties of Supercritical Fluids (SCFs) that make them technically enticing are their enhanced ability to dissolve organic compounds, an ability, which can be easily tuned by changing temperature and/or pressure, thus changing the fluid properties from gas-like to liquid-like. This sensitivity to temperature and pressure

leads to simple solute-solvent separation schemes. Other attractive features of SCFs include low viscosity and high diffusivity that are essential to reduce mass transfer resistance during the desorption processes. Because of these special characteristics, supercritical fluids are used in extraction, separation, chemical reaction, impregnation, polymer processing, food processing, environmental remediation and pharmaceutical production.[18] The most popular fluid is supercritical carbon dioxide (SC CO_2) because it is non-toxic, non-flammable, readily available, and inexpensive [17–19].

Like other new technologies, SFE technology utilizing CO_2 as a fluid has its specific problems. One of these problems is the limited ability of SC CO_2 to dissolve and separate polar or high molecular weight organic compounds even at very high densities. To develop SFE process efficiency, the selectivity and solubilizing power of SC CO_2 can be enhanced by the addition of polar organic compounds, known as modifiers.[20] The lack of fundamental information on the behavior of such mixtures on the remediation process leads to one of the goals of this study.

Experiments at different conditions (250 and 350 bar, 80 and 160 °C, and flow rates of 1 and 4 ml/min) were performed with pure and modified CO_2 to find the best extraction temperature, pressure and flow rate and type of modifier (heptane or toluene) added at 5% (v/v) to extract hydrocarbons from oil-contaminated sediments.

1.2. Supercritical fluid extraction (background)

1.2.1. Supercritical fluids

Fluids above their critical temperature and critical pressure are defined as supercritical fluids (SCFs). Within the supercritical region only one state-of-the-fluid exists and it

possesses both gas- and liquid-like properties. At this condition, the fluid will not be condensed by increasing the pressure.

The phase diagram for pure carbon dioxide illustrating the supercritical region is shown in Figure 1. On this diagram, C.P. represents the critical point and T.P. represents the triple point of the fluid. Outside the supercritical region, a single substance exists either as a solid, liquid, gas or as a coexistence of two or more phases. The carbon dioxide can no longer exist as a solid above a certain temperature but it can be a liquid or a gas. Given the temperature, if the external pressure is equal to the vapor pressure, the liquid is in equilibrium with the gas and the two phases coexist. Increasing the temperature leads to a rise in the equilibrium pressure delineating the vapor pressure curve. Moving along the curve to higher pressure and temperature values, the liquid becomes less dense because of the effect of thermal expansion and the gas becomes denser due to the effect of increasing pressure. Eventually the densities of the liquid and gas phases become identical (called critical density, ρc) at the critical point and the substance becomes a supercritical fluid where the distinction between the gas and the liquid disappears.[21] Therefore, when carbon dioxide, for example, is heated and compressed above its critical point (critical temperature, T_c = 31.3°C, and critical pressure, P_c=73.9 bar) the substance will be in a pure supercritical fluid phase.[22]

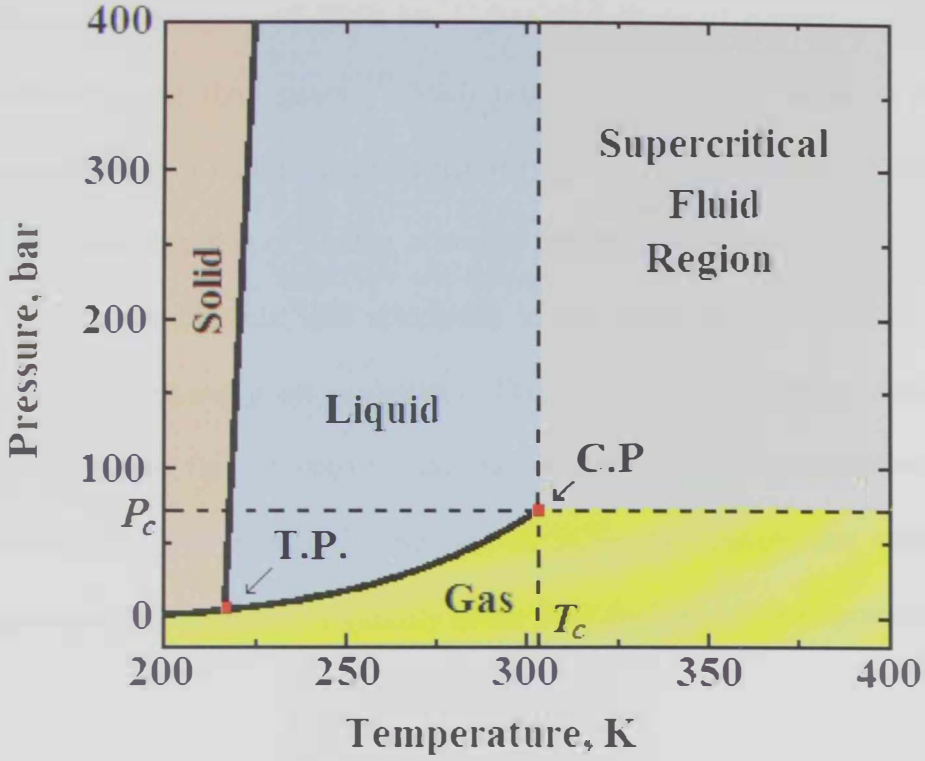

Figure 1: Phase diagram of pure carbon dioxide.

Supercritical fluids can be changed to a gas or liquid state by simply adjusting the temperature and pressure. This flexibility in the operating conditions and liquid-like to gas-like properties makes supercritical fluids suitable for extraction applications.

Supercritical Fluids (SCFs) can have better mass transfer through a porous matrix due to their higher diffusivity than a normal liquid phase, resulting in a faster extraction. Moreover, densities of SCFs are higher than those of normal gases, leading to higher solvent power than gases.[23] Such properties allow the SCFs to dissolve and carry materials like a liquid but also enter very small pores like a gas. Viscosities of SCFs are also lower than that of liquids, allowing for better transportation. The values of densities, diffusion coefficients, and viscosities in the supercritical region are between those of typical liquids and gases as shown in Table 1. Finally, separation of the contaminant from the extraction fluid is usually much easier in the case of a supercritical fluid than a liquid solvent. This is because in the case of SCFs the contaminant separates easily as the pressure drops, since its solubility in the fluid declines at lower pressures.

Table 1: Comparison of physical properties of SCFs, a typical gas and liquid.[24]

Phase	**Gas**	**SCF**	**Liquid**
Diffusion Coefficient (cm^2/s)	10^{-1}	10^{-3}	10^{-5}
Density (g/cm^3)	10^{-3}	0.2 - 0.9	1.0
Viscosity (mPa·s)	10^{-2}	10^{-2} - 10^{-1}	1.0

1.2.2. Supercritical carbon dioxide

Several fluids can be theoretically used for supercritical fluid extraction. Table 2 presents some compounds that can be used as supercritical fluids including their critical parameters (critical temperature (T_c), critical pressure (P_c) and critical densities (ρc)). Among all these fluids, CO_2 has so far been the most widely used one. This is due to its convenient critical parameters (critical pressure of 73.9 bar and critical temperature of 31.3 °C). This means that the use of CO_2 for the extraction does not require significant energy in order to keep the fluid at the supercritical state. Moreover, CO_2 is considered as an environmentally benign solvent that can have a number of positive impacts on extraction, such as solvent replacement, energy efficiency and better separations. Being nonflammable, nontoxic and inexpensive, CO_2 is preferred over solvents that are carcinogenic, environmentally hazardous, volatile, or legislatively regulated. Moreover, supercritical CO_2 has zero heat of vaporization [25] ; therefore the solvent can be easily and completely removed by depressurization, eliminating the energy-intensive drying process generally used to remove traditional solvents. Depressurization and recompression schemes allow for easy separation from other chemical components and therefore recycling.

The polar character of the carbon dioxide as a solvent is intermediate between a truly non-polar solvent such as hexane and weakly polar solvents. Carbon dioxide is often classified as a non-polar solvent, but it has some limited affinity with polar solutes because of its large molecular quadrupole.[26] To improve its affinity with polar molecules further, polar co-solvents or modifiers are sometimes added to CO_2.

Table 2: Critical parameters of some useful compounds as SCFs.[27]

Substance	T_c (°C)	P_c (MPa)	ρ_c (10^3 Kg/m^3)
CO_2	31.30	7.39	0.47
N_2O	36.50	7.35	0.45
SF_6	45.50	3.76	0.74
NH_3	132.50	11.40	0.24
H_2O	374.00	23.00	0.34
n-C_4H_{10}	152.00	3.80	0.23
n-C_5H_{12}	197.00	3.78	0.23
Xe	16.60	5.92	1.10
$CC_{12}F_2$	112.00	4.13	0.56
CHF_3	25.90	4.75	0.52

1.2.3. Supercritical fluid extraction of hydrocarbons from sediments

A growing concern has arisen in recent years about the fate of hazardous compounds, notably petroleum products in sediments. Soil/sediment is often a receptacle of these compounds, and there is potential danger that contaminates may reach the groundwater in their original or altered composition but still preserving toxic properties. Decontamination of soil/sediment by solvent extraction is usually carried out by adding organic solvents into soil/sediment to extract the toxic compounds. However, this method tends to create another problem for the environment as the solvent cannot entirely be removed from the matrix.

Supercritical fluids have been used as extraction media to remove various types of substances from solid matrices. The original application of the supercritical fluid extraction technology was for the recovery of various compounds from different natural sources or for environmental purposes, which are still widely studied.[13]

Carbon dioxide is a compound that shows a relatively mild critical point (73.9 bar and 31.3 °C), not requiring an excessive amount of energy to reach supercritical conditions. In addition to the low cost of the carbon dioxide, its high chemical stability and lack of toxicity, make it a popular solvent for extracting hydrocarbons from rocks, sediment and mud slurries. Therefore, extraction using SC CO_2 is preferred over solvent extraction to remove the harmful compounds from soil/sediment. Although SCF technology has been successfully realized for environmental remediation in the laboratory, its commercialization still lacks the significant technological improvement required in order to reach economic feasibility.

Significant research has been carried out in order to study and investigate various aspects of contaminant removal by SC CO_2. Comprehensive presentations of various aspects on the use of this technology for extraction purpose are available in several

critical reviews [28-41] and hundreds of other scientific articles. Several of these articles discuss the extraction of various organic compounds from various matrices for the remediation of environment by supercritical fluid extraction (SFE) technique.

Pressure, temperature, composition of the crude oil and physicochemical properties of the solid matrix affect the extraction capacity of SC CO_2. Supercritical CO_2 has been successfully used for extracting a variety of organic compounds such as polycyclic aromatic hydrocarbons (PAHs),[38-44] polychlorinated biphenyls (PCBs),[41,45-49] pesticides,[50-52] and hydrocarbons.[53-59] The extraction of these compounds was performed from various porous media, such as soils and/or sediments,[53,60-62] or rocks.[53,59] These investigators have studied a combination of different parameters such as characteristics of the supercritical fluid (with and without modifier), solid matrix, thermodynamic and kinetic conditions (i.e. temperature, pressure, density, and flow rate), water content and solute physical and chemical properties, in order to find the optimum conditions leading to the highest extraction yield.

Data for CO_2 extraction at extremely high pressures and temperatures, which represent some United Arab Emirates (UAE) reservoir conditions such as Bu Hasa reservoir (274 bar, 121 °C) are scarce in the literature, especially for oil-saturated sediment (or rocks). Al-Marzouqi investigated the capacity of SC CO_2 to extract hydrocarbons from a typical UAE sediment saturated with crude oil (in the absence of water) under a wide range of pressures and temperatures. Extraction efficiencies greater than 70 % were obtained for the extraction of hydrocarbons from a typical UAE sediment saturated with crude oil at 300 bar and 120 °C.[53] In the present study, the effects of temperature (80 and 160 °C), pressure (250 and 350 bar), modifier (heptane and toluene) and CO_2 flow rate (1 and 4 ml/min) on the extraction capacity of the SCF and on the composition of extracted hydrocarbons were investigated.

1.2.4. Factors affecting SFE processes

Most of the SFE studies of contaminants from soils and sediments were based on the desorption phenomena associated with spiked and native bound solutes in soils/sediments. The acquired data from experiments and modeling show that many parameters can affect SFE processes such as: characteristics of SCFs and solid matrix, thermodynamic and kinetic conditions (e.g. temperature, pressure, density, and flow rate), water content, solute physical and chemical properties, etc.[40] To select a distinctive set of best conditions under these circumstances for an efficient SFE process is a difficult task. However, in this study the effect of characteristics of SC CO_2 (with and without modifiers) and the thermodynamic and kinetic conditions on the extraction efficiency of the SCF was the main goal.

1.2.4.1. Effect of flow rate

Flow rate of a Supercritical fluid can affect both solute desorption rate and final residual concentrations. The effect of flow rate on SFE rates has been used to determine whether the extraction is limited primarily by analyte solubility and retention of analytes on matrix active sites (i.e. the solubility/elution process) or by the desorption/kinetic process.[63] The extraction rates controlled primarily by the solubility/elution process showed direct correlation with SFE flow rates while the extraction rates for samples that are controlled primarily by the kinetics of the initial desorption step showed little or no change with different SFE flow rates.[40]

1.2.4.2. Effect of temperature and pressure (density)

The solubility of a substance is determined by two factors: its volatility and the solvating effect of the fluid. The solvating effect of the fluid depends on the fluid density; therefore, the density of a SCF affects its capacity to extract hydrocarbons during the SFE

process. This is why thermodynamic parameters such as temperature and pressure, which affect the density, are considered the main factors influencing the SFE process.

Effect of Temperature

It is generally accepted that temperature affects the SFE efficiency by changing both the thermodynamic (density) and kinetics of the process. For a constant pressure, the density of a SCF decreases with increasing temperature. Therefore, the solvating effect of the fluid decreases as temperature is increased. But the volatility of the solute increases as the temperature increases at constant pressure. As a result, the solubility of a substance in a supercritical fluid at constant pressure first decreases with the increase in temperature as the density effect of the SCF is dominant, then the substance solubility reaches a minimum, after which the solubility increases with temperature as the volatility effect takes over. Therefore, we can conclude that, there are opposite effects of temperature on SFE such as decreasing fluid density and hence, the solute recovery on one hand, and increasing solute solubility through its vapor pressure, on another hand.

The temperature corresponding to the minimum solubility varies with pressure and the solute type. For solutes of limited volatility the minimum solubility occurs at a high temperature and may never be seen experimentally. Thus, for relatively nonvolatile species, increasing the temperature of the SCF at constant pressure will result in a reduction in its density and thus the solubility of the extract, i.e. hydrocarbons, in the fluid, leading to reduced extraction efficiencies. But, in many examples where the solute is more volatile, efficiencies improve as temperature is increased despite the reduction in fluid density.[61]

Effect of Pressure

Gaseous CO_2 has a density of 0.001808 g/ml at 25 °C and atmospheric pressure. Under these conditions it is not very effective as a solvent for liquids and solids; however, as pressure is increased, which causes an increase in density, the extractive power of CO_2 improves.[57] Therefore, the solubility of organic compounds in CO_2 increases at higher density. Moreover, the CO_2-oil interfacial tension is expected to decrease with the increase in pressure as a result of the increase in CO_2 density. This effect was shown for the CO_2-ethanol system, for which the density of the CO_2 was the only influencing parameter on the interfacial tension.[64]

1.2.4.3. Characteristics of SCFs

The unique physicochemical properties of SC CO_2 make it an ideal fluid for SFE except for one weakness: having no net dipole moment, CO_2 is an ineffective solvent for dissolving polar or high molecular weight compounds even at very high pressures. The modifier, also called entrainer or cosolvent, is a conventional organic solvent added to supercritical CO_2 to improve the extraction yield through certain mechanism such as enhancing analyte solubility, covering the matrix active sites and inhibiting the desorpted solute's re-adsorption, matrix-swelling or in situ derivatization.[65] A wide variety of modifiers has been evaluated by different investigators for enhancing extraction efficiency including methanol, toluene, pyridine, triethylamine, pyrrolidine, hexane, acetone, chloroform, methylene chloride, tributylphosphate, and ethyl acetate. Librando and others,[66] for example, used three modifiers: n-hexane, methanol and toluene at a concentration of 5% of the extraction fluid to extract Polycyclic Aromatic Hydrocarbons (PAH) compounds from marine sediments. According to Yang [67] the modifier effects are dependent on the sample matrix and modifier type when environmental samples are

extracted with SC CO_2 alone or modified with 10 vol. % methanol, diethylamine, or toluene.

Although there is no definite theory that enables one to select and optimize a modifier for supercritical fluid extraction, it appears that modifiers should be selected based on both type of the matrix and the target solute, i.e. extract characteristics.[68] Therefore, the modifiers that should be used in this study must be any liquid hydrocarbon that is miscible with the oil in the sediment.

1.2.5. Mechanisms of SFE processes

The recovery of organic pollutants from environmental samples, by supercritical fluid extraction process, requires three main steps: partitioning of the targeted solutes from the sample into SCF, removal from the extraction vessel, and collection of the extracted compounds. Studying the extraction recovery of SCF from spiked samples is an excellent method to develop the final two steps. However, it was observed experimentally, that SFE conditions that yield quantitative recoveries of spiked solutes may not be suitable for the extraction of the same compounds from real-world samples.[40] Because of the heterogeneous nature of environmental samples, the partitioning step may be controlled by solute solubility in SCF, kinetic limitations, and/or the ability of the SCF to interrupt matrix–solute interactions. These interactions that control SFE rates from heterogeneous environmental samples are not well understood yet.[40] Therefore, It should be kept in mind that the results from spiked recovery process are often not valid for determining extraction efficiencies from complex real-world samples such as soils and sediments, but such studies can draw a general scheme of the SFE process.

The mechanisms of decontamination by SFE are similar to the solvent extraction. Basically, the extraction fluid is pumped through the contaminated sediment. Driven by the concentration gradient, the contaminant to be removed moves from the grains, where

it is deposited or adsorbed, to the fluid. The solvent, whether it is a liquid or a supercritical fluid, transports the contaminant out of the matrix. Finally, the fluid is usually recovered and separated from the contaminant as shown in Figure 2. Therefore, solvent power and transport properties of the fluid phase play an important role in the extraction process.

In order to interpret the obtained results, the extraction phenomena should be first understood. The extraction process involves four main stages: desorption of oil from the solid grain inside the sediment particles, intraparticle diffusion of the oil, transfer of oil from the external sediment surface to the bulk fluid through a thin layer, and the transport of oil along the solid bed. Density and viscosity of the supercritical fluid play a major role in this four-stage extraction process.

The solvating power of supercritical CO_2 is proportional to its density; the higher the density, the more substrate the CO_2 can extract from the matrix.[69] It was indicated that CO_2 density is an essential factor in the CO_2-oil extraction.[64] Even though the density of a supercritical fluid increases with pressure and becomes liquid-like, the viscosity and diffusivity remain between liquid-like and gas-like values. The viscosity of the SC fluid gives the fluid the ability to penetrate the matrix; the lower the viscosity, the faster the fluid can penetrate the matrix. Additionally, supercritical fluids exhibit almost zero surface tension, which allows facile penetration into microporous materials. The combination of these properties of the SC CO_2 can be affected by factors such as temperature and pressure, which can have a significant influence on the extraction efficiency of SC CO_2.

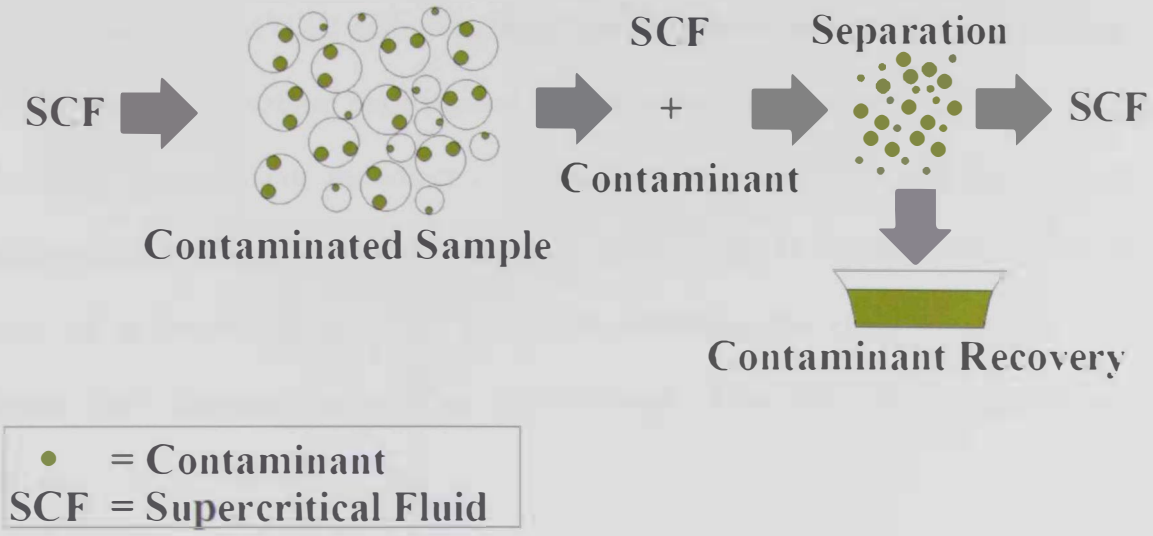

Figure 2: General scheme of a supercritical fluid extraction process.

1.3. Thesis objectives

Sediment contamination by petroleum products causes significant concerns in many parts of the world, especially in industrial areas. Studying the efficiency of pure and modified SC CO_2 in extracting hydrocarbons from sediment and from rock samples is very important for environmental reasons. The objective of this research is to gain deeper understanding of the capacity of pure and modified CO_2 under supercritical conditions to remediate contaminated UAE sediments from petroleum hydrocarbons. In particular, it is of our interest (1) to perform experimental measurements of extraction efficiency of the SFE process to investigate the effect of temperature, pressure, flow rate, and type of modifier added at 5% (v/v) on the capacity of the SCF, (2) to determine the extent of residual oil in the matrix after SFE and (3) to investigate the effect of particle type (sediment and limestone) and size on the efficiency of the SFE process at reservoir conditions (120 °C, 300 bar).

1.4. Outline of chapters

Chapter 2 discusses the experimental materials and methods used in this study including the experimental design, details of the apparatus, procedures and the scheme followed for the accomplishment of the present research.

Chapter 3 includes the results and discussions. First, results of the statistical analysis are presented. Then, the extraction results at different conditions are presented and the effects of different parameters are discussed. Also, the results of analyses used to investigate the extent of residual oil in the sediments after the SFE process are presented and discussed. Finally, the conclusions are included in Chapter 4.

CHAPTER 2

MATERIALS AND METHODS

CHAPTER 2

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2.1. Materials

Carbon dioxide (purity of 99.995%) was supplied by Abu Dhabi Oxygen Company. The crude oil (average molecular weight = 281.5 g/mole and density = 0.8634 g/ml) used in this work was obtained from Bu Hasa oil field (Abu Dhabi, UAE) and was filtered to remove all sand particles. This oil was stock tank oil (dead oil) not live reservoir oil. Hydrocarbon composition of the crude oil used in this study indicates the presence of mainly light and moderate hydrocarbons, i.e. 80 % hydrocarbons less than C_{20} (Figure 3).

The chemical modifiers (n-heptane and toluene) and the organic solvents (dichloromethane and methanol) were of analytical grade with purity ≥99% and were supplied by Sigma Aldrich. Sediment samples (bulk density = 1.6 g/ml and average particle size = 150 μm) were collected from Sahel oil field, which is near Bu Hasa oil field in the UAE. The particle size distribution of the sediment sample is shown in Figure 4. The size distribution of the sediment sample was: 11% less than 106 μm, 29.56% between 106 and 150 μm, 44.07% between 150 and 212 μm, 12.52% between 212 and 300 μm, 2.81% between 300 and 600 μm, 0.03% between 600 and 850 μm, and 0.01% between 850 to 1180 μm.

The porosity and permeability of the sediment were 35 % and 20.15 Darcy, respectively (Table 3).[70] The sediment sample used in this study was classified as silty sand according to Petijohn method. Compositional characteristics of the sediment are shown in Table 4. Fossilferous limestone rock sample (bulk density = 2.5 g/ml) was collected from Jabel Hafeet in Al-Ain City (UAE). The limestone rock was crushed to three different size range (small: ≤106 μm, medium: same size and distribution as the

sediment samples, large: 300 to 600 μm) to see the effect of particle size on the extraction capacity of SC CO_2.

The porosity and permeability of the small limestone particles were 25 % and 19.34 Darcy, respectively, while those for the medium limestone particles were 53 % and 5.78 Darcy and for the large limestone particles were 55 % and 4.33 Darcy (Table 3).[70]

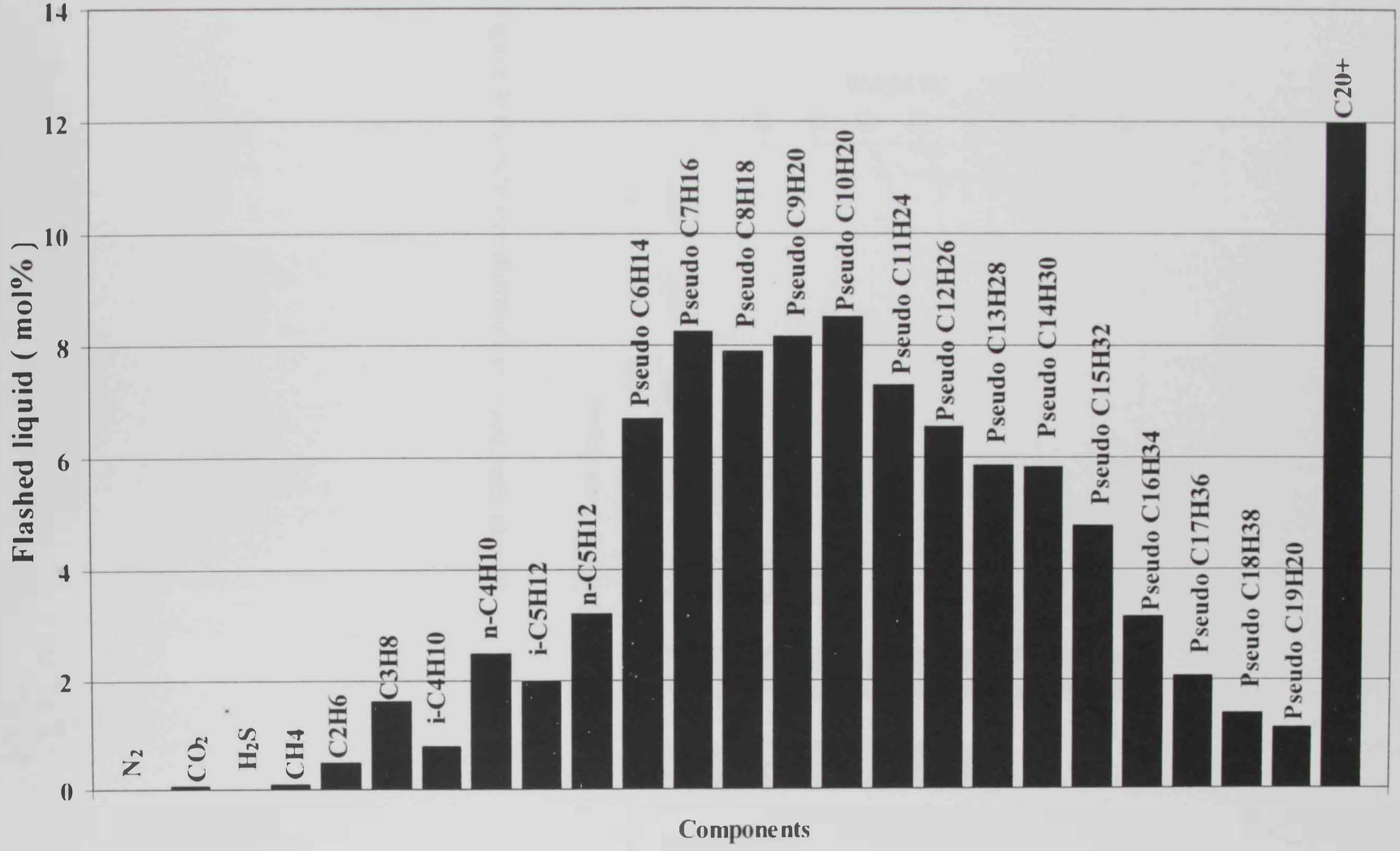


Figure 3: Bu Hasa crude oil composition.

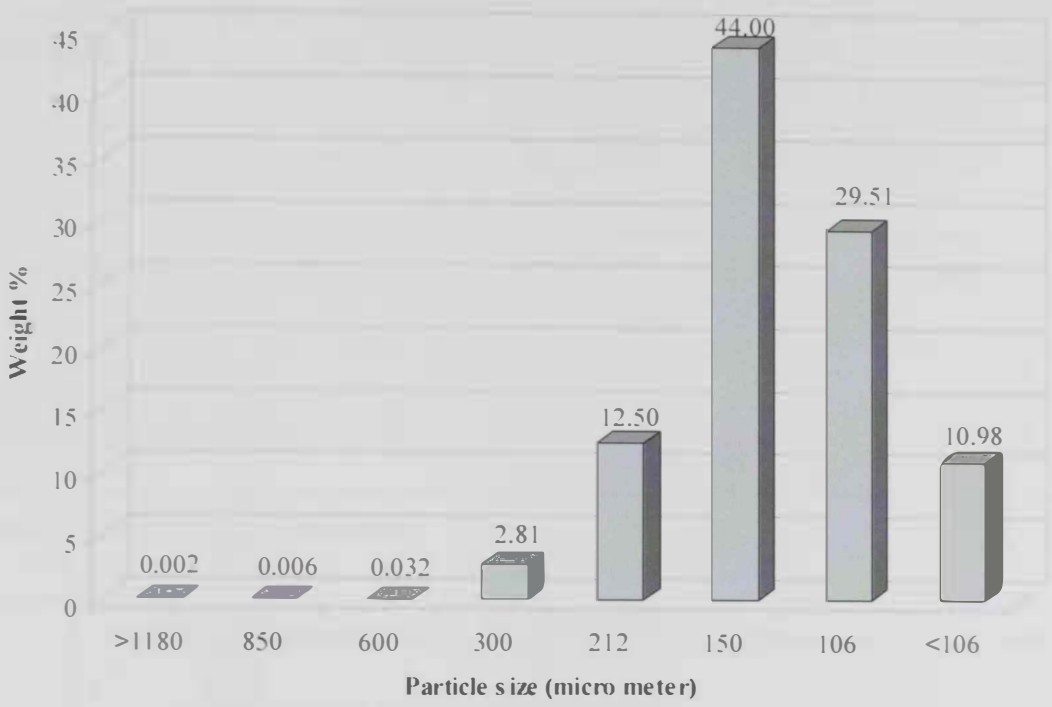


Figure 4: Particle size distribution of sediment sample.

Table 3: Properties of soil and limestone particles.

Property	Soil	Limestone (small)	Limestone (medium)	Limestone (large)
Particle size (μm)	150	≤106	150	300-600
Porosity (%)	35	25	53	55
Permeability (Darcy)	20.15	19.34	5.78	4.33

Table 4: Sediment sample characteristics.

Composition	Percentage	Comments
Quartz	> 97%	Quartz mostly is yellow- brown, glassy and milky, sub-angular to well rounded grains.
Sand	86.52 %	
Silt	13.48 %	
Clay	0.0%	
The other minerals are mostly: feldspar, rock fragments, heavy mineral grains		

2.2. Methodology

This section describes the experimental design, details of the apparatus used, procedures and the scheme followed for the accomplishment of the present research.

2.2.1. Experimental design

An experimental strategy was developed to identify the important factors out of many process variables, understand relationship between factors, optimize the extraction process and to test the robustness of the process. The use of experimental designs and of statistics provided a powerful framework to draw objective conclusions from limited number of experiments. Extraction of hydrocarbons with SCF from contaminated sediment was carried out by following the full factorial experimental design with four factors. The factors investigated were (in parentheses are the variable coded values): pressure with values of 250 (−1) and 350 (1) bar, temperature 80 (−1) and 160 (1) °C, flow rate of 1 (−1) and 4 (1) ml/min and fluid type pure SC CO_2 (1), modified SC CO_2 with 5% (v/v) toluene (2) and modified SC CO_2 with 5% (v/v) n-heptane (3). This design was used to find the best conditions for the extraction of oil from contaminated sediment and to study the effects of all factors (temperature, pressure, flow rate of SCF, and type of modifier) on the extraction efficiency. The total number of factor-level combinations was 24. Each experiment was repeated twice, resulting in a total number of 48 experiments.

Experiments were run in random order to eliminate various types of biases due to uncontrolled nuisance factors. The statistical analysis was performed using the statistical package SPSS (SPSS inc., Version 15.0). Table 5 shows the order of the experiments and the factor-level combinations. All the statistical analyses of the effects of variables on the extraction efficiency were performed using a multi-way analysis of variance (ANOVA)

with two replications per cell. Also, whenever applicable, Tukey's HSD Test was used to identify the factor-level combinations that yield the extraction efficiency.

The CO_2 extraction efficiency (the ratio of extracted hydrocarbons to the initial amount of crude oil in place) is used throughout this study to evaluate the capacity of CO_2 to extract hydrocarbons from the solid matrix, i.e. sediment and rock.

Table 5: Experimental order and factor-level combinations.

Experiment order	Temperature	Pressure	Flow Rate	Modifier
10	−1	1	1	1
34	−1	1	1	1
43	1	1	−1	1
40	1	−1	1	1
46	1	1	1	1
28	−1	−1	1	1
25	−1	−1	−1	1
4	−1	−1	1	1
16	1	−1	1	1
22	1	1	1	1
13	1	−1	−1	1
1	−1	−1	−1	1
19	1	1	−1	1
31	−1	1	−1	1
7	−1	1	−1	1
37	1	−1	−1	1
18	1	−1	1	3
6	−1	−1	1	3
21	1	1	−1	3
33	−1	1	−1	3
30	−1	−1	1	3
45	1	1	−1	3
42	1	−1	1	3
27	−1	−1	−1	3
39	1	−1	−1	3
24	1	1	1	3
3	−1	−1	−1	3
12	−1	1	1	3
15	1	−1	−1	3
9	−1	1	−1	3
36	−1	1	1	3
48	1	1	1	3
26	−1	−1	−1	2
41	1	−1	1	2
35	−1	1	1	2
29	−1	−1	1	2
38	1	−1	−1	2
11	−1	1	1	2
5	−1	−1	1	2
20	1	1	−1	2
8	−1	1	−1	2
2	−1	−1	−1	2
47	1	1	1	2
14	1	−1	−1	2
23	1	1	1	2
17	1	−1	1	2
44	1	1	−1	2
32	−1	1	−1	2

* Factors code: Temperature (80 °C = −1and 160 °C = +1), Pressure (250 bar= −1 and 350 bar = +1), CO_2 flow rate (1 ml/min= − 1 and 4 ml/min= +1), Fluid type (Pure SC CO_2 = 1, Pure SC CO_2 + 5 % (v/v) toluene = 2, pure SC CO_2 + 5 % (v/v) heptane = 3).

2.2.2. Experimental apparatus

Figure 5 shows the schematic diagram of the experimental setup for supercritical fluid extraction used in this study. The experimental apparatus consisted of a 260 ml capacity syringe pump and a controller system (ISCO 260D), and an ISCO series 2000 SCF Extraction system (SFX 220) consisting of a dual-chamber extraction module with two 10-ml stainless steel vessels. The syringe pump was equipped with a temperature control jacket, which was connected to tap water and was used for cooling the pump cylinder when it was filling with CO_2. Operating pressure of the syringe pump ranged from 1 to 517 bar with an accuracy of 0.5% and the flow rate ranged from 0.001 to 107 ml/min, also with an accuracy of 0.5%. Displacement resolution of the syringe pump was 16.6 μl.

The display panel of the pump controller system displayed the pressure, flow rate, time and volume of CO_2 in the cylinder. The extraction chamber of the SFX system had a temperature control of up to 150 °C. Since the extraction chamber was small (10 ml), some modifications were made on the system in order to use a ten times larger extraction chamber (100 ml) also made of stainless steel (DBR-JEFRI 100-10-BE). This chamber was kept in an oven (Memmert ULE 400) to control its temperature.

The oven had air circulation and a temperature control ranging from 30 to 250 °C with a precision of 0.1 °C. Pressure within the extraction chamber was measured and controlled by the ISCO system, while the temperature of the extraction chamber was measured and controlled by the oven.

An independent J-type thermocouple (Omega model JMTSS-062-U-12) was used to confirm the surface temperature of the extraction chamber. This thermocouple was connected to a temperature controller (Omega CN9000A) which displayed the temperature at the surface of the extraction chamber. A coil of tubing (about 1.5 m long, 1/16 in. stainless steel tubing) was used in the oven before the inlet of the extractor to

ensure the equilibrium temperature of the solvent prior to entering the extraction chamber.

In order to have a good control of the flow rate, a micrometer valve (HIP 15-12AF1-V) was used as the expansion valve at the exit of the extraction chamber. A J-type thermocouple (Omega model JMTSS-062-U-12) was fitted to the surface of this expansion valve, and the valve was heated using a heating tape (Omega model FWH171-060). The thermocouple and the heating tape were connected to a temperature controller (Omega CN9000A) which controlled and displayed the temperature of the expansion valve. The temperature of the expansion valve was kept at the same value as that of the extraction chamber. The precision of the temperature measurements for both the extraction chamber and the expansion valve was 0.1 °C. A cold trap containing circulating methanol was used to capture high temperature hydrocarbons while separating CO_2 from other components of the mixture.

Methanol was cooled to −15 °C using a chiller (Ultra-Kryomat, type K50D, No. D00210, Messgeräte-Werk Lauda, Germany) equipped with a circulating pump. After separating the extracted hydrocarbons from CO_2 in the cold trap, the CO_2 was exhausted to a ventilating hood.

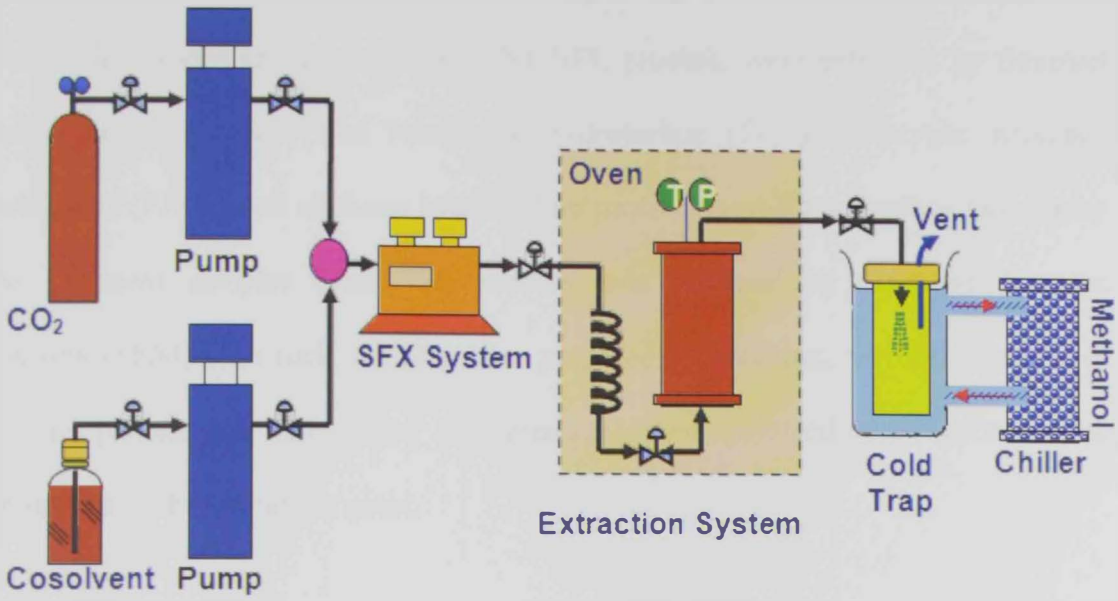


Figure 5: Experiment setup for supercritical fluid extraction.

2.2.3. Experimental procedures

The experimental procedure includes three steps, preparation of samples, supercritical fluid extraction, analysis of extracts and residues as shown in Figure 6. The sediment samples were prepared by spiking with crude oil followed by SFE process. Extraction yield and composition of aliphatic hydrocarbons in the extracts were determined. The residual hydrocarbons in the sediment, after SFE process, were extracted by Soxehlet extraction to analyze for Total Petroleum Hydrocarbon (TPH), Polycyclic Aromatic Hydrocarbons (PAHs) and aliphatic hydrocarbon profile. In addition, surface topography of the sediment samples after SFE process was obtained by Scanning Electron Microscopy (SEM). The rock samples were prepared by crushing, sieving, selection of appropriate particle size and spiking with crude oil, then, followed by SFE process and determination of the extraction yield.

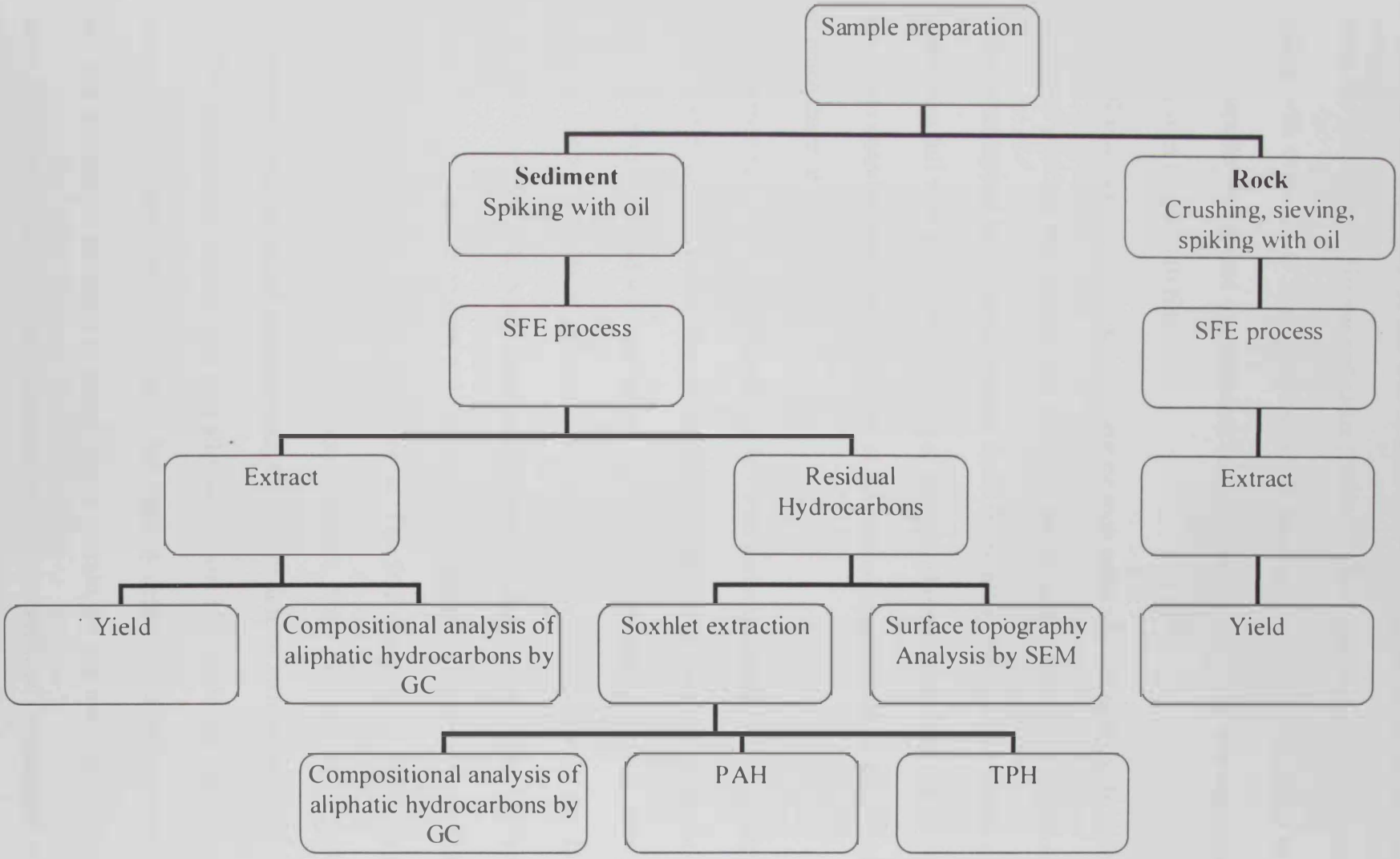


Figure 6: Experimental procedure.

2.2.3.1. Extraction of hydrocarbons by SFE process

Extraction efficiency of the SC CO_2 process was studied on sediment/rock samples using the procedure of Hwang and Ortiz (2000).[57] Each sediment/rock sample (65 g) was spiked with crude oil (6.5 g) and was mixed thoroughly in a beaker. About 60 g of the spiked sample was placed in a stainless steel cylinder holder with two caps fitted with a stainless steel (mesh 200) filter.

In all runs, the initial oil to sediment or rock ratio was 10 w/w %. In order to have consistent packing, the sample was added to the sample holder using a spatula and the holder was tapped on a bench counter three times after each sample addition until the holder was full with approximately 60 g of sample. The sample holder was inserted in the extraction chamber and kept in the oven at the desired temperature for at least 30 minutes to reach thermal equilibrium.

Meanwhile, the syringe pump was filled with carbon dioxide from a supply cylinder. In the case of modified CO_2, the second syringe pump was used to deliver the cosolvent (heptane or toluene), which was mixed with the CO_2 stream at desired ratio. Pure and modified carbon dioxide at supercritical condition was then added to the ISCO SCF Extraction system (SFX system) and equilibrated for about 15 minutes. The temperature of the SFX system was maintained at the same temperature as the oven which had the extraction chamber that contained the sample. The SCF was allowed to flow through the coil of tubing and enter the extraction chamber from the bottom. The fluid was equilibrated with the spiked sediment/rock sample for at least 30 minutes.

The supercritical solution was then allowed to flow into a cold dry trap vial, where the extract was separated from the supercritical fluid by depressurizing the system. The flow rate was maintained manually at about 1 or 4 ml/min, by the micrometering expansion valve. Flow rate of the SCF was measured by the movement of the piston in the syringe

pump and displayed on the ISCO controller system. Therefore, the recorded flow rate of 1 or 4 ml/min is the flow rate of liquid CO_2 at the system pressure. The temperature of the depressurizing valve was kept at 70 °C. The hot extracted hydrocarbons were collected in the cold dry vial and the CO_2 was sent to a ventilating hood. The temperature of the cold dry trap was kept at –15 °C. The cold methanol was circulated into a plastic cylinder where the vial was held.

For the runs with pure CO_2, mass of the extract collected in the vial was measured at different volumes of CO_2 (15, 25, 35, 50, 100, 150, 200, 300 and 400 ml) passed through the sample. For the runs with modified CO_2, mass of the extract collected in the vial was only measured at 400 ml of the SCF passed through the sample. At the end of the experiment (after 400 ml of the fluid was passed through the sample), the extraction process was stopped and the pressure in the extraction chamber was slowly dropped to atmospheric pressure.

After the completion of each SFE experiment, the extracted hydrocarbons were dissolved in dichloromethane and the volume was completed to 25 and 50 ml for the pure and modified CO_2 runs, respectively. For the runs with modified CO_2, concentration of the modifier in the extract was measured by Gas Chromatography. All extracts and sediment samples after SFE process were stored in a refrigerator until analysis.

A typical extraction run took about 7-9 hours for the conditions at the slow flow rate of 1 ml/min, while it took about 2-3 hours for the conditions at the fast flow rate of 4 ml/min. The mass of the CO_2 passed through the sample was calculated from the volume recorded on the ISCO controller system and the density calculated from operating pressure and the temperature of the cooling water using NIST Chemistry WebBook.

The extraction efficiency (the ratio of extracted amount of oil to the initial amount of oil in place) was used throughout this study to evaluate the capacity of pure and modified

CO_2 to extract crude oil from the solid matrix. The effects of operating parameters (i.e. temperature, pressure, CO_2 flow rate and mass of CO_2 passed through the sample) and modifier on the extraction efficiency and composition of extracted hydrocarbons were investigated.

2.2.3.2. Analyzing the residual oil in the extracted sediment samples

The residual oil remaining in selected sediment samples after extraction by SC CO_2, was removed from the sediment matrix by soxhlet extraction using 250 ml of dichloromethane. The sediment sample was refluxed until the thimble containing the sample become clean. Then it was dried in the oven at 55 °C overnight. Composition of the residual oil was analyzed by a GC and compared to that of the original oil and the extract determined from supercritical CO_2 extraction.

Scanning Electron Microscopy (SEM) images of the sediment samples after SFE process were used to study the ability of the SC CO_2 to extract hydrocarbons and reduce the residual hydrocarbons during the extraction process. Additional investigation for some of the main pollutant parameters, such as TPH and PAH, was conducted on the remaining sediment after the extraction process. These investigations were also undertaken to assess the technique's efficiency to remediate contaminated UAE-sediments. All these analyses were performed by the Central Laboratory Unit (CLU) at the United Arab Emirates University and the procedures are described in the following sections.

2.2.3.2.1. Scanning Electron Microscopy (SEM)

In this study the SEM (JEOL 5600) with secondary electron detector (topographical observation of surface), backscattared electron detector (compositional observation of surface) and X-ray detector (elemental analysis of spacemen) was used. The specimen

surface was coated by fine coater (JFC-1200) to form a metal film for the electrical conductivity. Then the sample was scanned at different magnifications and the images were analyzed.

2.2.3.2.2. Determination of Total Petroleum Hydrocarbons (TPH)

The term total petroleum hydrocarbons (TPH) describes a large family of several hundred chemical compounds that originally come from crude oil. Due to the various chemicals present in crude oil and in other petroleum products, it is not practical to measure each one separately in a contaminated environment. However, it is helpful to measure the total amount of TPH at a site.

TPH may enter our environment through accidents, from industrial releases, or as byproducts from commercial or private uses. Some of the TPH compounds can affect our health by harming the central nervous system. For example, some compounds at high levels in the air can cause headaches and dizziness. Other compounds can cause a nerve disorder called "peripheral neuropathy" consisting numbness in the feet and legs. Other TPH compounds can cause effects on the blood, immune system, lungs, skin, and eyes.

Determination of TPH provides information on the contamination of sediment with petroleum products. TPH measurement is an estimate of the amount of hydrocarbons present in the sample, which are mainly hydrocarbons with carbon numbers ranging from C_8 to C_{40}. This range of carbon extends from the volatile hydrocarbon compounds with the lower boiling point to the non-volatile compounds found at the higher boiling point range.

In this study, about 5 g of the homogenized sediment was placed in a 50 ml beaker; the sample was acidified to pH = 2 with approximately 0.1 ml of concentrated hydrochloric acid (HCL) 1:1. Then 5 g $MgSO_4$ was added to the acidified sample and stirred to create a smooth paste. The paste was spread on the sides of the beaker and left

for about 15-30 minutes at room temperature until the material was solidified. The solids were transferred to a mortar and grinded to a fine powder. The powder was then added to paper extraction thimble. Both the beaker and the mortar were wiped with pieces of filter paper moistened with solvent and the paper was added to the thimble. The thimble was placed in a soxhlet apparatus and extracted using n-haxane. The rate and time of extraction in the soxhlet apparatus were strictly controlled to extract different greases having varying solubilities. After removing the solvent, the extraction cup which contained the residue (TPH) was cooled and removed. The cup was kept in a desiccator and weighed. Finally, the TPH was calculated (mg/Kg) from the weight of residue and the sample.

2.2.3.2.3. Determination of Polycyclic Aromatic Hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) are group of chemical compounds that consist of fused aromatic rings and do not contain heteroatoms or carry substituents. PAHs occur in oil and are of concern because some compounds have been identified as carcinogenic, mutagenic, and teratogenic.

PAHs are lipophilic, which means that they mix more easily with oil than water. PAHs can be found in the environment mainly in sediment, sediment and oily substances. Natural crude oil contains significant amounts of PAHs, arising from chemical conversion of natural products, such as steroids, to aromatic hydrocarbons. They are also found in processed fossil fuels, tar and various edible oils. Therefore, PAHs are one of the most widespread organic pollutants.

The PAH analysis was used in this study to determine the concentration of certain hydrocarbons in the sediment. These include 16 common pollutant PAHs: Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Benzo(a)anthracene, Chrycene, Benzo(b)fluoranthene, Benzo(k)fluoranthene,

Benzo(a)pyrene, Dibenzo(a,h)anthracene, Benzo(g,h,I)perylene and Indeno(1,2,3-cd)pyrene. These PAHs were extracted from sediment with (50:50 hexane:acetone) by using soxhlet extraction method. The solvent was then carefully evaporated under nitrogen. Then a 20 µl aliquot of the extract was injected into an HPLC. The HPLC apparatus was Waters 2695 Alliance Separation Module, Waters 474 Scanning Fluorescence Detector coupled with Waters 486 UV Detector and Waters Millennium 32 Chromatographic Manager workstation. The HPLC column used in this study was a chromosphere-3PAH column (100*4.6 mm ID, 3 µm). The 16 PAH compounds were detected by ultraviolet (UV) and fluorescence detectors simultaneously.

2.2.3.2.4. Hydrocarbon profile of extracts and residues

Gas chromatography (GC) was used to analyze the aliphatic hydrocarbon composition of the original crude oil, the extracted hydrocarbons and the residual hydrocarbons in contaminated sediment after supercritical fluid extraction. The gas chromatograph (Chrompack, CP9001) was equipped with a 50 m × 0.32 mm CP-SIL 5CB with DF = 1.2 µm fused silica capillary column. Nitrogen gas was used as transport media (carrier gas). The analysis by GC was programmed to hold the temperature of oven for 2 min at 40 □C, heating from 40 to 275 °C at 5 °C/min and then for 151 min at 275 °C. A split mode of injection was applied for the analysis of original crude oil and the SFE extracts. However, due to the low concentration of hydrocarbons in the residual oil, a splitless mode was applied for the analysis of all residual oils.

CHAPTER 3

RESULTS AND DISCUSSION

CHAPTER 3

RESULTS AND DISCUSSION

3.1. Introduction

This work aims to investigate the ability of SC CO_2 to extract sediment contaminants, i.e. petroleum hydrocarbons. The extractions were carried out utilizing pure SC CO_2 and chemically modified SC CO_2, i.e. addition of 5 % (v/v) of n-heptane or toluene. Different SFE conditions were used to study the influence of the pressure, temperature and CO_2 flow rate on the extraction efficiency and composition of the extracted hydrocarbons and residual hydrocarbons in the sediment. Each set of operating conditions were repeated twice, resulting in a total number of 48 runs. Appendix I includes the raw data for these 48 runs. In addition, the ability of SC CO_2 to extract hydrocarbons at reservoir conditions (300 bar, 120 °C) was investigated on rock samples of different particle size and on the sediment sample. The CO_2 extraction efficiency is calculated according to the following equation and used throughout this study to evaluate the capacity of CO_2 to extract crude oil from oil-saturated sediment/rock at different pressures and temperatures:

$$Extraction\ efficiency\ (\%) = \frac{mass\ of\ extracted\ oil}{initial\ mass\ of\ oil\ in\ the\ soil\ sample} \times 100$$

3.2. Statistical analysis

The operating conditions that were investigated on the sediment samples and the average value of the efficiencies at each set of operating conditions are summarized in Table 6. Moreover, values of density, viscosity and kinematic viscosity of pure CO_2 at the pressures and temperatures used in this study were calculated using NIST Chemistry WebBook (Table 6) in order to investigate their influence on the SFE process. Although

both density and viscosity of CO_2 always increase with pressure and decrease with temperature, the combined property (kinematic viscosity) does not show a constant effect with pressure and temperature. The temperature and pressure combinations employed in this study were: 250 and 350 bar at 80 and 160 °C (Table 6). The lowest value of extraction efficiency (68.38% ± 1.99) with an addition of 5 % toluene was obtained at 250 bar and 160 °C, while the maximum efficiency (92.26 % ± 5.40) was found at 350 bar and 80 °C with an addition of 5 % n-heptane. The highest efficiency obtained by SC CO_2 alone (without fluid type) was 78.51 % ±0.46, which was obtained at 350 bar and 160 °C. The large variation in the susceptibility of crude oil to the extraction by SC CO_2 is believed to be attributed to the complexity of crude oil mixture containing tens of thousands of saturated and aromatic hydrocarbons and no-hydrocarbon compounds with significantly different physico-chemical properties that vary with temperature and pressure.

Table 6: Properties and average extraction efficiencies of supercritical fluid for sediment samples.

Temperature (°C)	Pressure (bar)	CO_2 flow rate (ml/min)	Modifier 5% (v/v)	CO_2 density (g/ml)	CO_2 viscosity (μPa·s)	CO_2 kinematic viscosity × 10^8 (m^2/s)	Average extraction efficiency (%) ± SEM*
80	250	1	–	0.68622	56.03	8.17	72.32 ± 0.49
80	250	4	–	0.68622	56.03	8.17	75.07 ± 0.92
80	350	1	–	0.78897	70.376	8.92	77.76 ± 0.78
80	350	4	–	0.78897	70.376	8.92	77.40 ± 0.55
160	250	1	–	0.39294	33.905	8.63	68.44 ± 0.43
160	250	4	–	0.39294	33.905	8.63	69.03 ± 1.47
160	350	1	–	0.52948	43.726	8.26	78.51 ± 0.46
160	350	4	–	0.52948	43.726	8.26	77.91 ± 0.37
80	250	1	n-Heptane	–	–	–	80.40 ± 2.96
80	250	4	n-Heptane	–	–	–	79.51 ± 2.99
80	350	1	n-Heptane	–	–	–	92.26 ± 5.40
80	350	4	n-Heptane	–	–	–	87.68 ± 1.20
160	250	1	n-Heptane	–	–	–	73.03 ± 2.18
160	250	4	n-Heptane	–	–	–	78.23 ± 4.66
160	350	1	n-Heptane	–	–	–	85.07 ± 0.55
160	350	4	n-Heptane	–	–	–	82.91 ± 5.02
80	250	1	Toluene	–	–	–	76.05 ± 2.58
80	250	4	Toluene	–	–	–	71.65 ± 1.43
80	350	1	Toluene	–	–	–	77.63 ± 3.30
80	350	4	Toluene	–	–	–	81.01 ± 0.56
160	250	1	Toluene	–	–	–	72.35 ± 3.02
160	250	4	Toluene	–	–	–	68.38 ± 1.99
160	350	1	Toluene	–	–	–	70.38 ± 0.15
160	350	4	Toluene	–	–	–	70.13 ± 2.38

*SEM: Standard Error of the Mean

The statistical analysis was based on a full factorial model with four factors (temperature, pressure, flow rate and fluid type) with two replications per cell. A four-way analysis of variance (ANOVA) was used, where the response was the raw extraction efficiency value and the four factors were temperature, pressure, flow rate and fluid type. A level of 5% was used as the cut-off value for statistical significance.

Results of the multi-way ANOVA based on the original values of extraction efficiency show that temperature, pressure and fluid type have significant effect on the extraction efficiency, but the flow rate of the CO_2 does not have a significant effect, i.e. Sig. >0.05 (Table 7). Moreover, pressure and fluid type interact. This means that the effect of pressure depends on which fluid is used and vice versa, which is not the case with temperature. However, by checking the validity of the ANOVA model using residual analysis, the normality assumption was found to be satisfied, i.e. the p-value is higher than 5%. But, the homogeneity of variance assumption was found to be satisfied with respect to the factors flow rate, temperature and pressure, but it was not satisfied with respect to fluid type. This violation of the assumptions of ANOVA should not have adverse effects on the validity of the method because when the model is balanced (i.e., there are equal numbers of replications per cell) ANOVA is robust to such a violation.[71]

Table 7: Statistical analysis based on a multi-way ANOVA.

Source	Type III Sum of Squares	df*	Mean Square	F**	Sig.
Corrected Model	1760.595[(a)]	23	76.548	6.394	0.000
Intercept	283,086.096	1	283,086.096	23,646.971	0.000
Temperature	246.404	1	246.404	20.583	0.000
Pressure	458.761	1	458.761	38.322	0.000
Fluid Type	759.580	2	379.790	31.725	0.000
Flow Rate	2.316	1	2.316	0.193	0.664
Temperature * Pressure	0.906	1	0.906	0.076	0.786
Temperature * Fluid Type	36.043	2	18.021	1.505	0.242
Pressure * Fluid Type	86.269	2	43.134	3.603	0.043
Temperature * Pressure * Fluid Type	64.238	2	32.119	2.683	0.089
Temperature * Flow Rate	0.718	1	0.718	0.060	0.809
Pressure * Flow Rate	1.245	1	1.245	0.104	0.750
Temperature * Pressure * Flow Rate	2.800	1	2.800	0.234	0.633
Fluid Type * Flow Rate	7.423	2	3.712	0.310	0.736
Temperature * Fluid Type * Flow Rate	21.330	2	10.665	0.891	0.423
Pressure * Fluid Type * Flow Rate	66.958	2	33.479	2.797	0.081
Temperature * Pressure * Fluid Type * Flow Rate	5.604	2	2.802	0.234	0.793
Error	287.312	24	11.971		
Total	285,134.003	48			
Corrected Total	2,047.907	47			

(a) R Squared = 0.860 (Adjusted R Squared = 0.725)
* df: degrees of freedom.
** F: Test Statistic.

Figures 7 and 8 illustrate the effects of temperature and flow rate on the extraction efficiency, respectively. Figure 7 represents the mean value of extraction efficiency for 24 experiments at each temperature including bars showing the standard error of the mean. Similarly, the mean value of the extraction efficiency for 24 experiments at each flow rate is shown in Figure 8. Results indicate that flow rate does not affect the extraction efficiency while temperature has an inverse effect on the extraction efficiency.

Due to the interaction between pressure and fluid type, effect of these parameters can not be shown separately, therefore, Figure 9 shows the effect of both pressure and the fluid type on the extraction efficiency. Each point on Figure 9 represents the mean value of extraction efficiency for 8 experiments for each fluid type at a given pressure including bars showing the standard error of the mean. As shown in the figure, the extraction efficiency of pure and modified SC CO_2 increases as the pressure is increased. Moreover, the extraction efficiency of the modified SC CO_2 by 5% (v/v) heptane is higher than that of both pure SC CO_2 and modified SC CO_2 with 5% (v/v) toluene. However, due to the interaction between pressure and fluid type, the extraction efficiency of modified SC CO_2 with 5% (v/v) toluene is found to be higher than that for pure SC CO_2 at the low pressure (250 bar) but lower at the high pressure (350 bar).

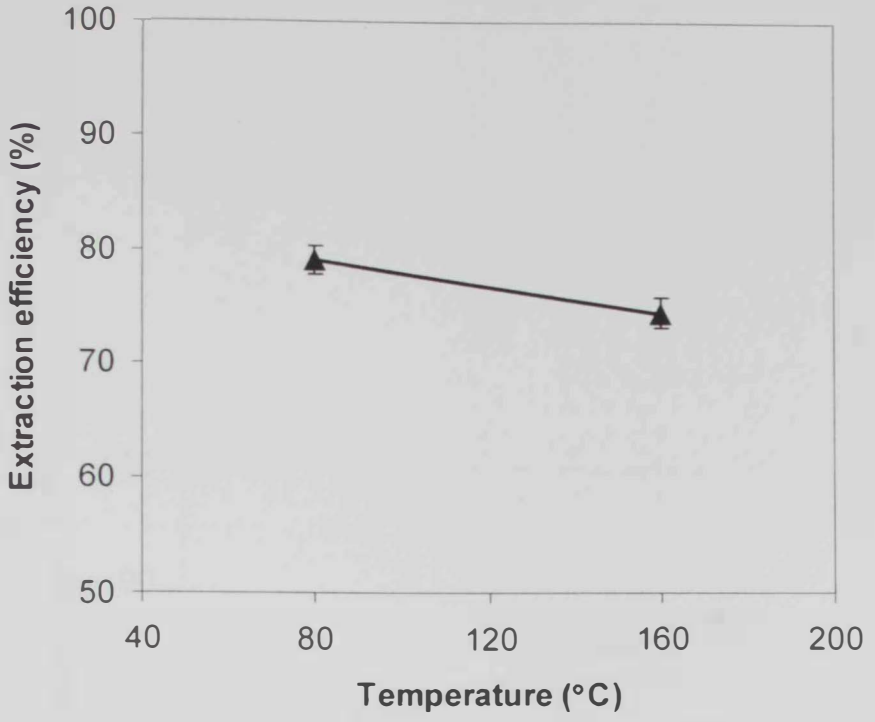


Figure 7: Effect of temperature on the extraction efficiency.

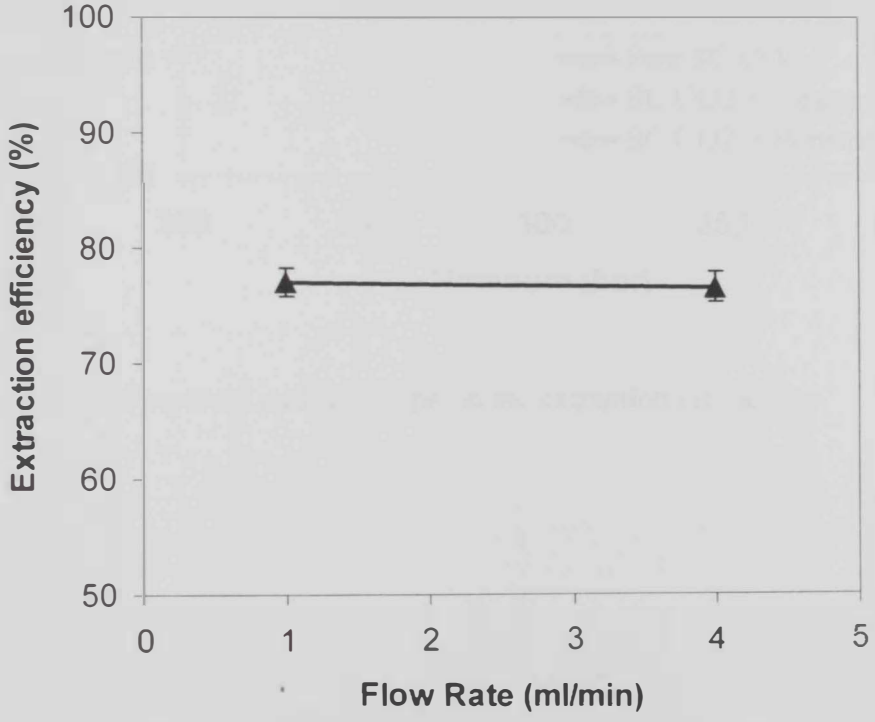


Figure 8: Effect of CO_2 flow rate on the extraction efficiency.

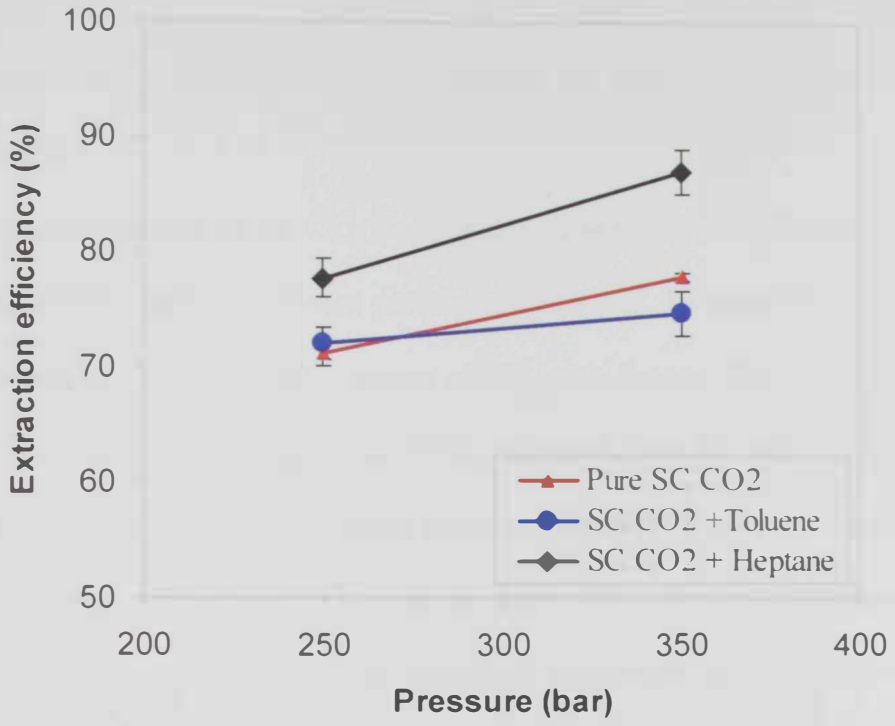


Figure 9: Effect of pressure and fluid type on the extraction efficiency.

3.3. Supercritical carbon dioxide extraction of hydrocarbons

In the following sections, the effects of CO_2 flow rate, temperature, pressure and modifier type on capacity of SC CO_2 for the extraction of hydrocarbons from sediment saturated with Bu Hasa crude oil are discussed. All runs exhibited a similar nonlinear trend for extraction efficiency vs. mass of CO_2 used. However, the initial slope and the final average value of extraction efficiency were different for the conditions investigated in this study. Moreover, additional experiments were conducted in order to investigate the effect of grain size (100 to 600 μm) and type (sediment and limestone) on the extraction capacity of SC CO_2.

The extraction efficiencies of SC CO_2 from sediment saturated with Bu Hasa oil are plotted to illustrate the effect of different parameters. Mass of the extracted oil and the CO_2 passed through the sample are also shown on the same figures. The results indicate that a high CO_2-oil ratio (about 10 g CO_2/g of oil, estimated from the slope of the linear part of the curve) is required in the extraction process. The CO_2-oil ratio obtained here is about 3 times higher than the reported value for successful CO_2 flooding projects.[64] However, the focus of this study was on the extraction mechanism at the CO_2-oil contact point and not on the displacement process.

3.3.1. Effect of flow rate

Decreasing the flow rate usually ensures more contact time and results in higher extraction efficiencies for a given amount of CO_2 used. However, saturation is achieved at certain flow rates, below which the flow rate does not affect the extraction efficiency of the solvent. Two flow rates (1 and 4 ml/min) were used in this study. Moreover, when evaluating the influence of the CO_2 flow rates, i.e. 1 and 4 ml/min, on the extraction capacity of the fluid from oil-saturated sediment, all extractions were carried out using

400 ml of the extraction fluid. Both flow rates were studied at all operation conditions as shown previously in Table 6.

The results presented in Figures 10 and 11 showed that the extraction efficiency was almost the same at both flow rates used in this study (1 to 4 ml/min). Therefore, the extraction process is independent of the CO_2 flow rate for the studied conditions and thus the extraction process should be operated at 4 ml/min in order to reduce the extraction time. The insignificant effect of flow rate on extraction efficiency is mainly due to the high extraction pressures (250 and 350 bar). Therefore, the extraction efficiency may vary with CO_2 flow rate if the extraction pressure is lower.

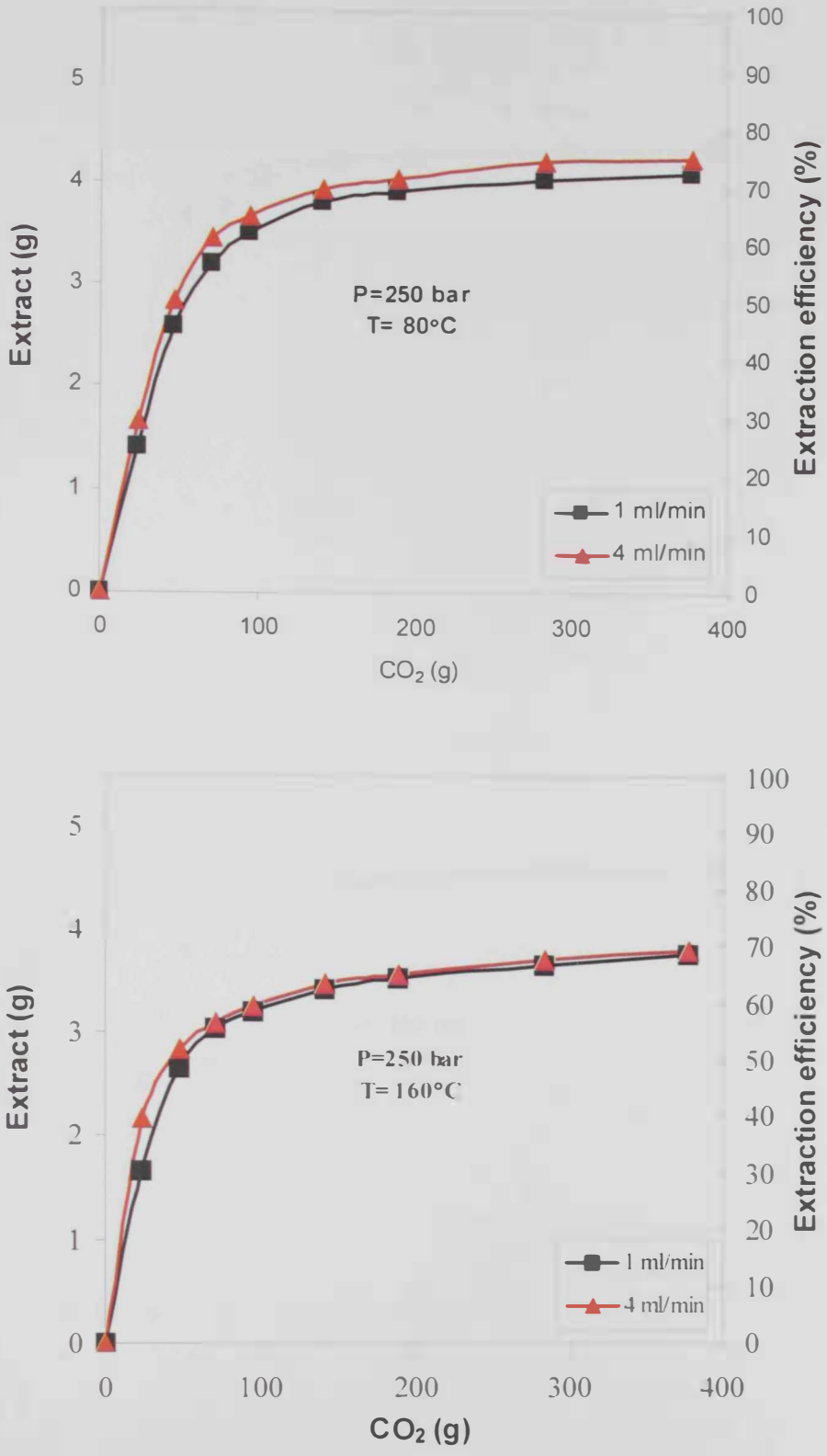


Figure 10: Effect of CO_2 flow rate on the extraction efficiency of pure SC CO_2 at 250 bar and two temperatures (80 and 160 °C).

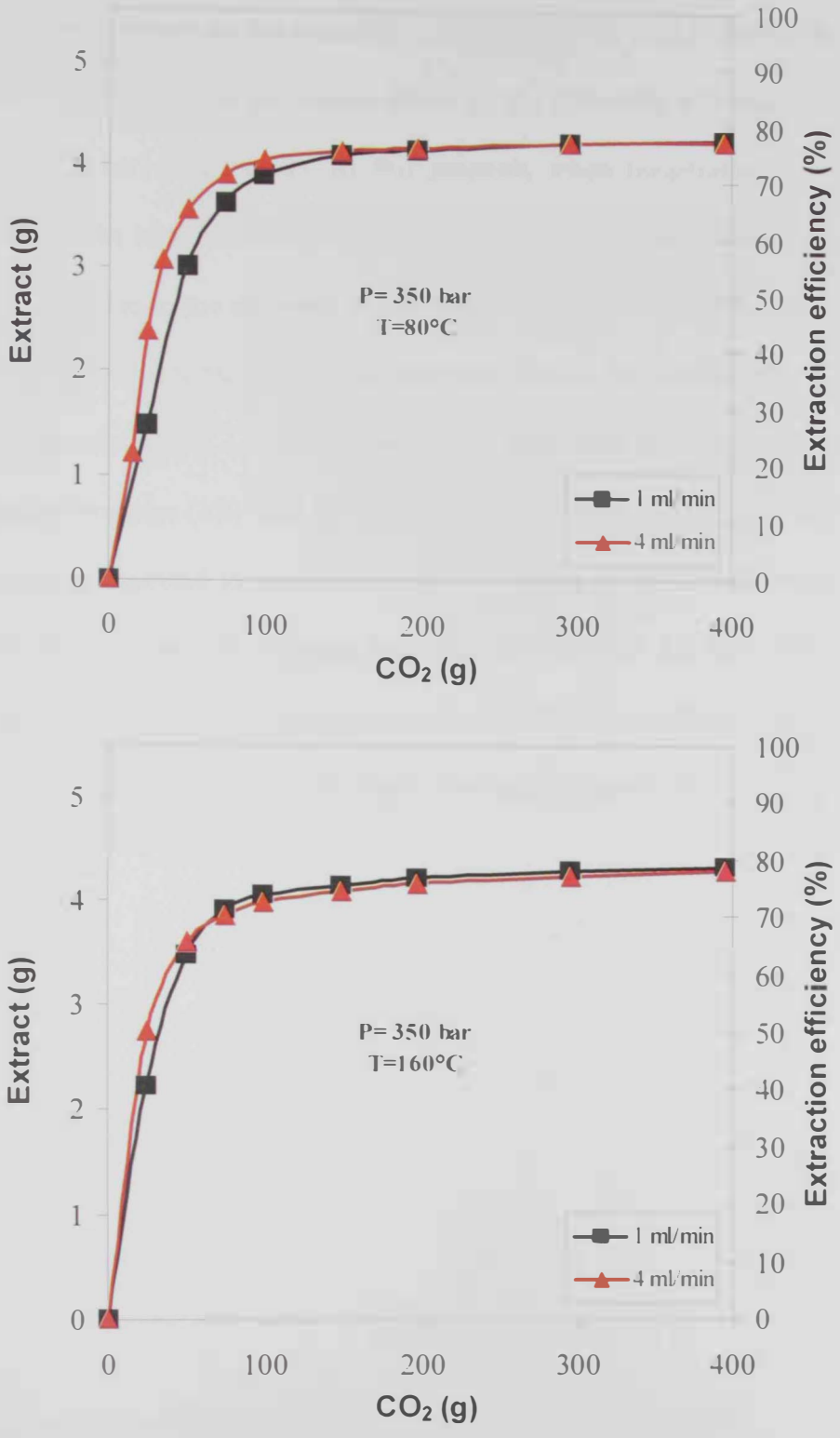
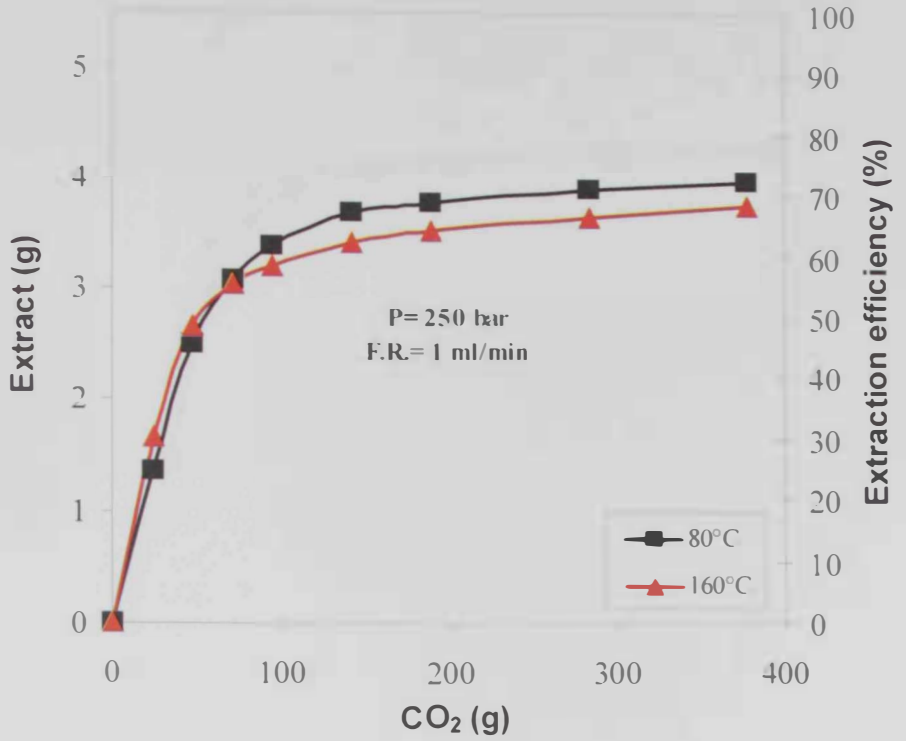


Figure 11: Effect of CO_2 flow rate on the extraction efficiency of pure SC CO_2 at 350 bar and two temperatures (80 and 160 °C).

3.3.2. Effect of temperature

The effect of temperature on the extraction efficiency of SC CO_2 is shown in Figures 12 and 13. The temperature had an inverse effect on the extraction efficiency of CO_2 at lower pressure (250 bar) (Figure 12). At this pressure, when temperature is increased from 80 to 160 °C, the kinematic viscosity increases by 5.6 % and interfacial tension is expected to increase due to the decrease in CO_2 density of 42.7 %. The increase in both kinematic viscosity and interfacial tension adversely affects the extraction capacity of CO_2 leading to approximately 4.9 % decrease in the extraction efficiency. On the other hand, at the higher pressure (350 bar), when temperature is raised from 80 to 160 °C, the interfacial tension is expected to change unfavorably (since the density decreases by 33 %) while the kinematic viscosity changes favorably (decrease by 7.3 %). Consequently, temperature has a negligible effect on the extraction efficiency of CO_2 (77.76 and 78.51 % for 80 and 160 °C, respectively at flow rate = 1 ml/min) (Figure 13).



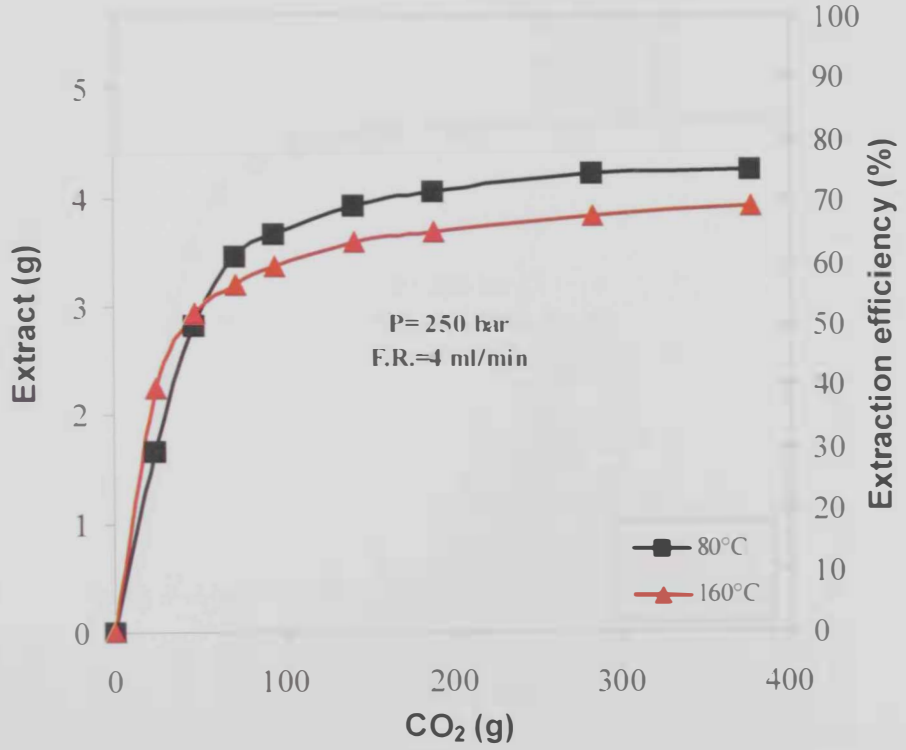


Figure 12: Effect of temperature on the extraction efficiency of pure SC CO_2 at 250 bar and two flow rates (1 and 4 ml/min).

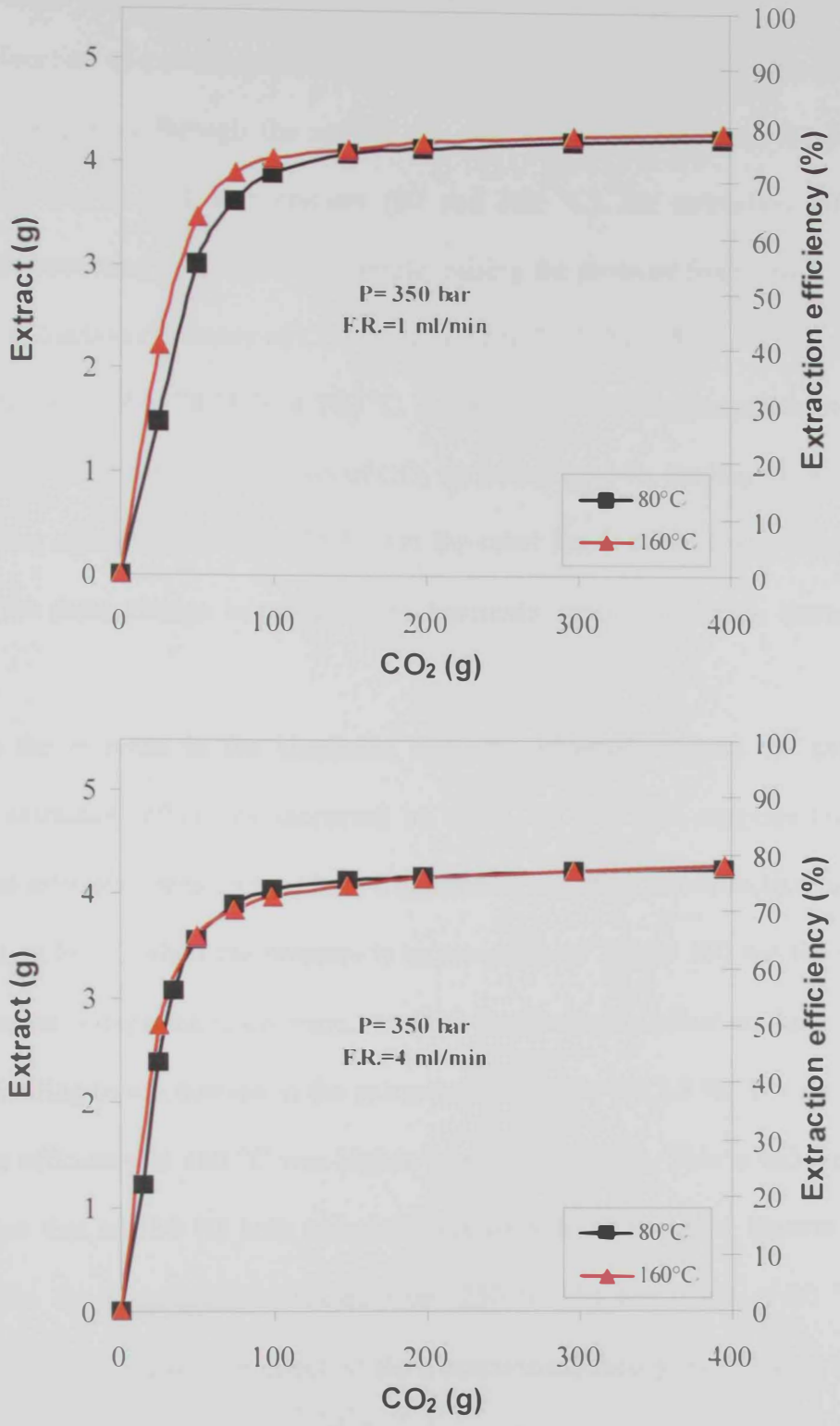


Figure 13: Effect of temperature on the extraction efficiency of pure SC CO_2 at 350 bar and two CO_2 flow rates (1 and 4 ml/min).

3.3.3. Effect of pressure

The extraction efficiencies of SC CO_2 from sediment saturated with Bu Hasa oil are plotted as a function of extraction pressure on Figures 14 and 15. Mass of the extracted oil and the CO_2 passed through the sample are also shown on the same figures. The results indicate that at both temperatures (80 and 160 °C), the extraction efficiency increased with increasing pressure. For example, raising the pressure from 250 to 350 bar increased the extraction efficiency of CO_2 from 72.32 to 77.76 % at 80 °C and flow rate 1 ml/min, and from 68.44 to 78.51 % at 160 °C. At 160 °C, when the pressure is increased from 250 to 350 bar, kinematic viscosity of CO_2 decreases by 4 %, leading to an increase in the extraction efficiency by about 15 %. On the other hand, at the lower temperature (80 °C), for the same change in pressure, the kinematic viscosity of CO_2 increases by about 9 %.

Although the increase in the kinematic viscosity adversely affects the extraction process, the extraction efficiency increased by about 7.5 %. This suggests that other factors such as interfacial tension may have a significant effect on the extraction process.

Therefore, at 80 °C when the pressure is increased from 250 to 350 bar the CO_2-oil interfacial tension is expected to decrease, resulting in a favorable effect on the extraction process and leading to an increase in the extraction efficiency by 7.5 %. The increase in the extraction efficiency at 160 °C was higher than that at 80 °C. This is believed to be due to the fact that at 160 °C both kinematic viscosity and interfacial tension change favorably when the pressure is increased from 250 to 350 bar while at 80 °C only interfacial tension has a favorable effect on the extraction efficiency for the same increase in pressure.

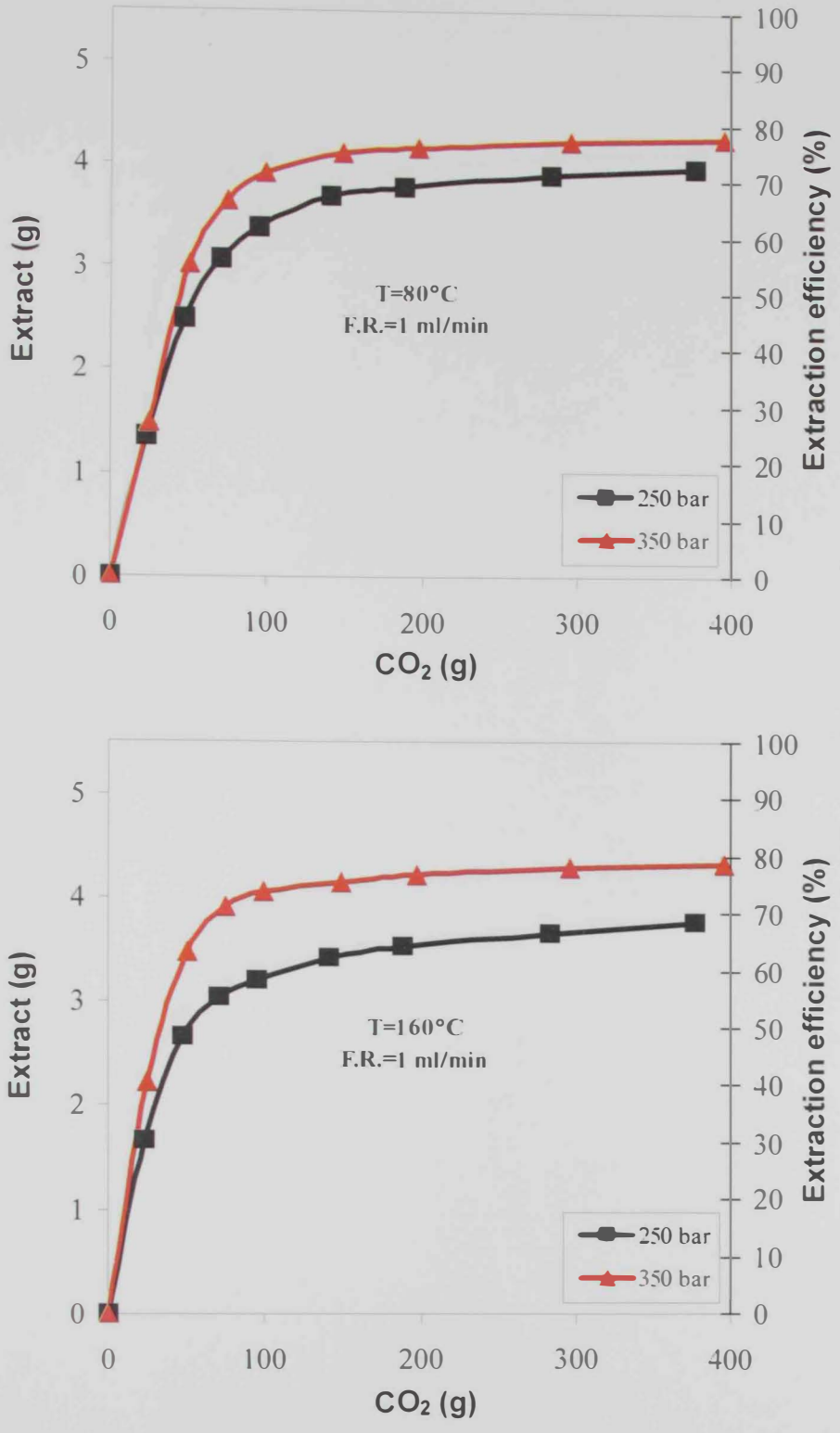


Figure 14: Effect of pressure on the extraction efficiency of pure SC CO_2 at two temperatures (80 and 160 °C) at CO_2 flow rate of 1 ml/min.

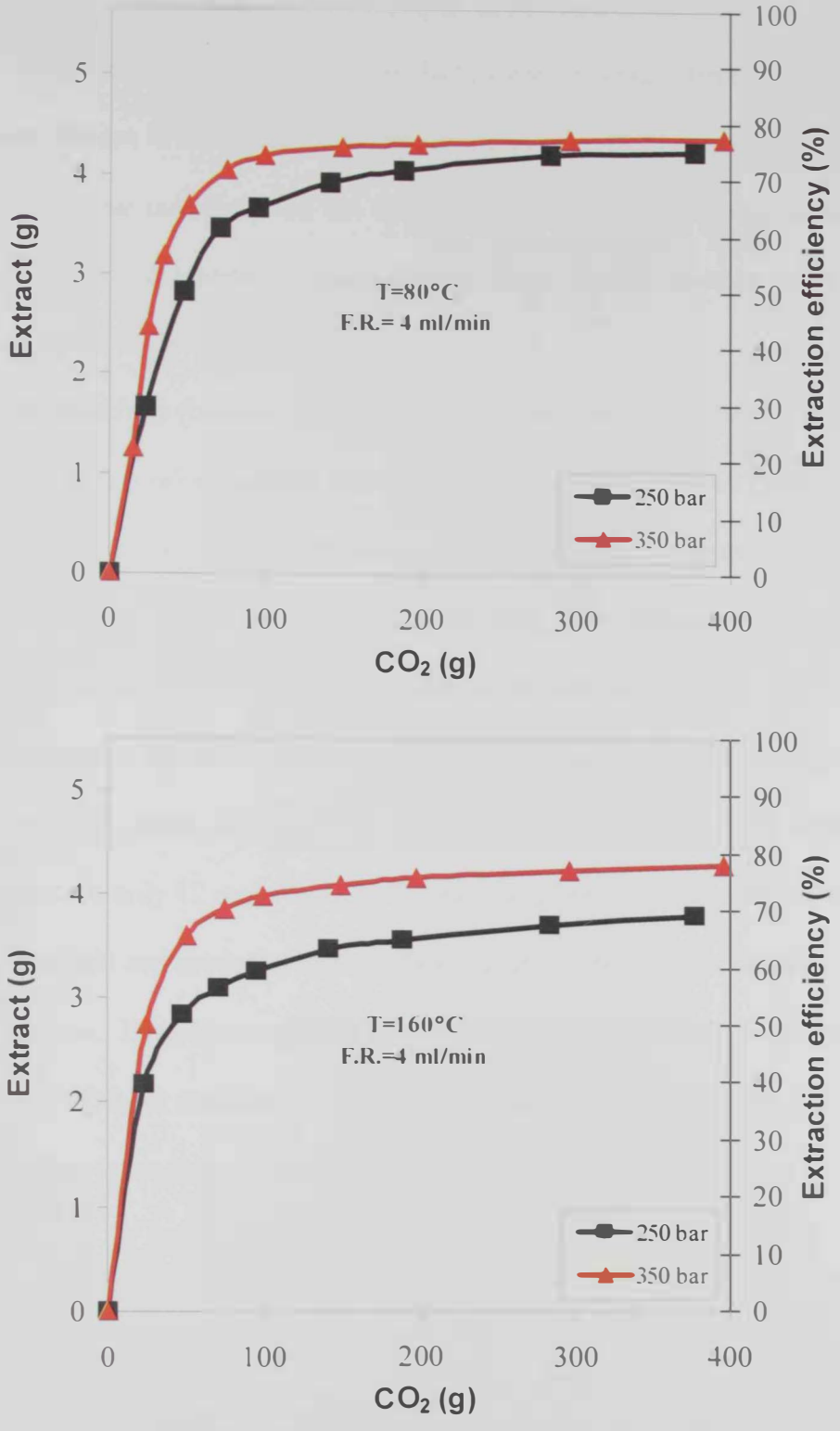


Figure 15: Effect of pressure on the extraction efficiency of pure SC CO_2 at two temperatures (80 and 160 °C) at CO_2 flow rate of 4 ml/min.

3.3.4. Effect of modifier

As evident from Figure 3 in section 1 of chapter 2, Bu Hasa crude oil, which was used in this study, contained significant amount of light hydrocarbons. Therefore, n-heptane and toluene were chosen as chemical modifiers for the SC CO_2 to investigate the effect of a polar and a non-polar modifier with the same carbon number. n-heptane, a non-polar aliphatic hydrocarbon, and toluene, an aromatic hydrocarbon with a polarity index of 2.4, have high solvency for hydrocarbons.

The effect of modifiers (heptane and toluene) on the extraction efficiency of SC CO_2 was studied when 5 % (v/v) a modifier was used to enhance the salvation power of CO_2. Based on the results shown in Figure 16, n-heptane shows that it is more effective than toluene in enhancing the extraction efficiency of SC CO_2. The increase in the efficiency when utilizing heptane can probably be attributed to the richness of Bu Hasa crude oil composition in aliphatic non-polar hydrocarbon compounds such as n-alkanes (C_6-C_{22}) as shown in Figure 3. The crude oil composition in Figure 3 illustrates that the compounds with C_{20} or higher are only 12 mole % of the Bu Hasa crude oil. In other words, Bu Hasa crude oil contains light and moderate hydrocarbons. These hydrocarbons dissolve more in heptane than toluene. Therefore, utilizing toluene results in lower extraction efficiency than when pure SC CO_2 or modified SC CO_2 with heptane is used. However, more study should be conducted to confirm these results.

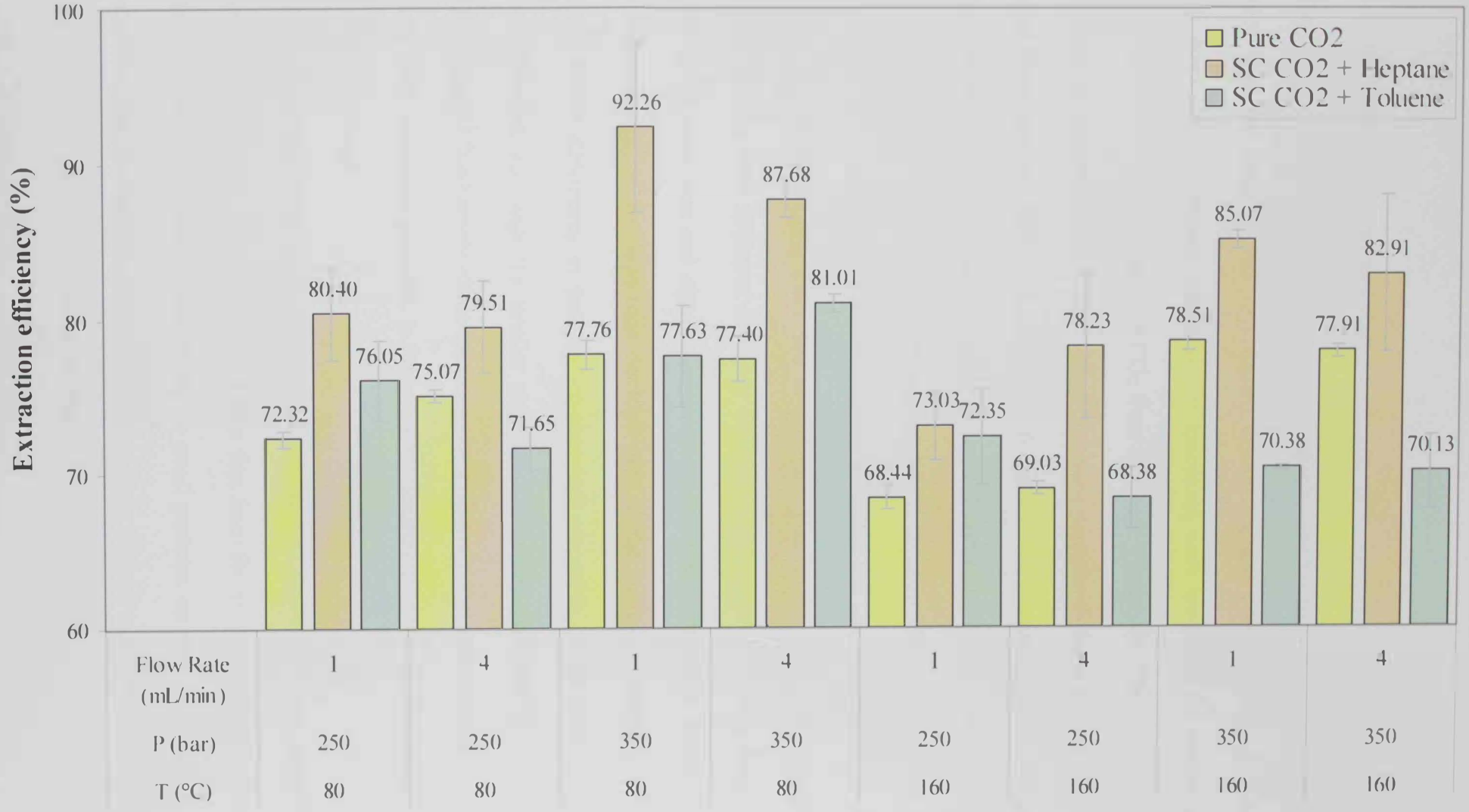


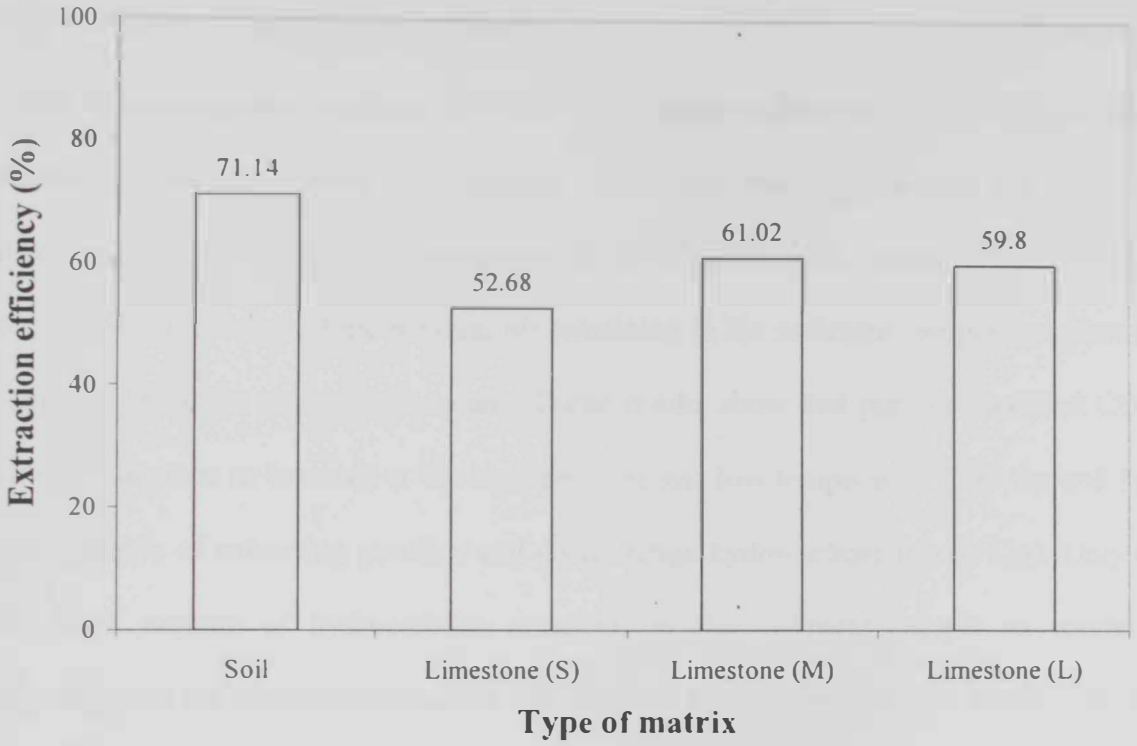
Figure 16: Average extraction efficiency for all runs.

3.3.5. Effect of particle type and size

The effect of particle size on the extraction capacity of CO_2 from limestone particles saturated with Bu Hasa oil was investigated at 300 bar and 120 °C. Three different particle sizes (small, medium, and large) of limestone were used and the results are compared to the extraction capacity of CO_2 from sediment (Figure 17). The medium size consisted of the same size and distribution of limestone particles as the sediment samples collected from Sahel oil field (11% less than 106 μm, 29.56% between 106 and 150 μm, 44.07% between 150 and 212 μm, 12.52% between 212 and 300 μm, 2.81% between 300 and 600 μm, 0.03% between 600 and 850 μm, and 0.01% between 850 to 1180 μm).

The small size consisted of limestone particles less than 106 μm, while the large size consisted of particles ranging from 300 to 600 μm. The results show that extraction efficiency of CO_2 from sediment is higher (by about 12%) than that from limestone particles of the same size and distribution (medium size), indicating that Bu Hasa oil holds more strongly to the limestone particles than to the sediment particles. This is attributed to the differences in the physico-chemical properties of the limestone and sediment samples. Although the smaller porosity of sediment compared to limestone particles (Figure 17) adversely affect the extraction efficiency, the higher permeability of sediment than limestone particles is believed to contribute to the higher extraction efficiency in sediment.

The medium and large limestone particles resulted in almost the same extraction efficiencies, which were about 15% higher than that from the small limestone particles. The lower extraction efficiency obtained for the small particles are most likely due to the larger surface area for the oil to hold to, making it more difficult to be removed from the surface and thus reducing the extraction efficiency.



Figuer 17: Effect of mtrix type and partical size on the extraction efficiency of pure SC CO_2 at reservior conditions (120 °C and 300 bar) at CO_2 flow rate of 1 ml/min. S = small size (≤106 μm), M = medium size (150 μm) and L = large size (300-600 μm).

3.4. The extract and the residual oil in the extracted sediment samples

The results of GC analysis for the extract and residue in sediment is presented and discussed. Moreover, the SEM, TPH and PAH analyses results are discussed, in order to achieve the second objective of this work.

3.4.1. Analysis of extracts and residues

Gas chromatographic analysis was used in this study to determine composition of the extracted oil and the residual oil remaining in the sediment samples after the SC CO_2 extraction process. The gas chromatograms of the original crude, extracted oil obtained from the SFE process, and the residual oil remaining in the sediment samples are shown in Figures 18-20 for representative runs. These results show that pure or modified CO_2 (with 5 % heptane or toluene) at the high pressure and low temperature (350 bar and 80 °C) is capable of extracting gasoline and diesel range hydrocarbons (up to C_{22}). Only a very small amount of hydrocarbons remained in the sediment sample as residue, suggesting that the supercritical fluid at this pressure and temperature can extract a wide range of hydrocarbons, in agreement with the results of extraction efficiency (Table 6).

The residual oil remaining in the sediment sample was not significantly different in the case of chemically modified CO_2 as compared with extraction by pure CO_2 at the same conditions. This might be due to the high density of SC CO_2 at the studied conditions (250 and 350 bar). Therefore, the enhancement in the solvating power of SC CO_2 by the addition of 5 % heptane or toluene was not very significant at these high pressures.

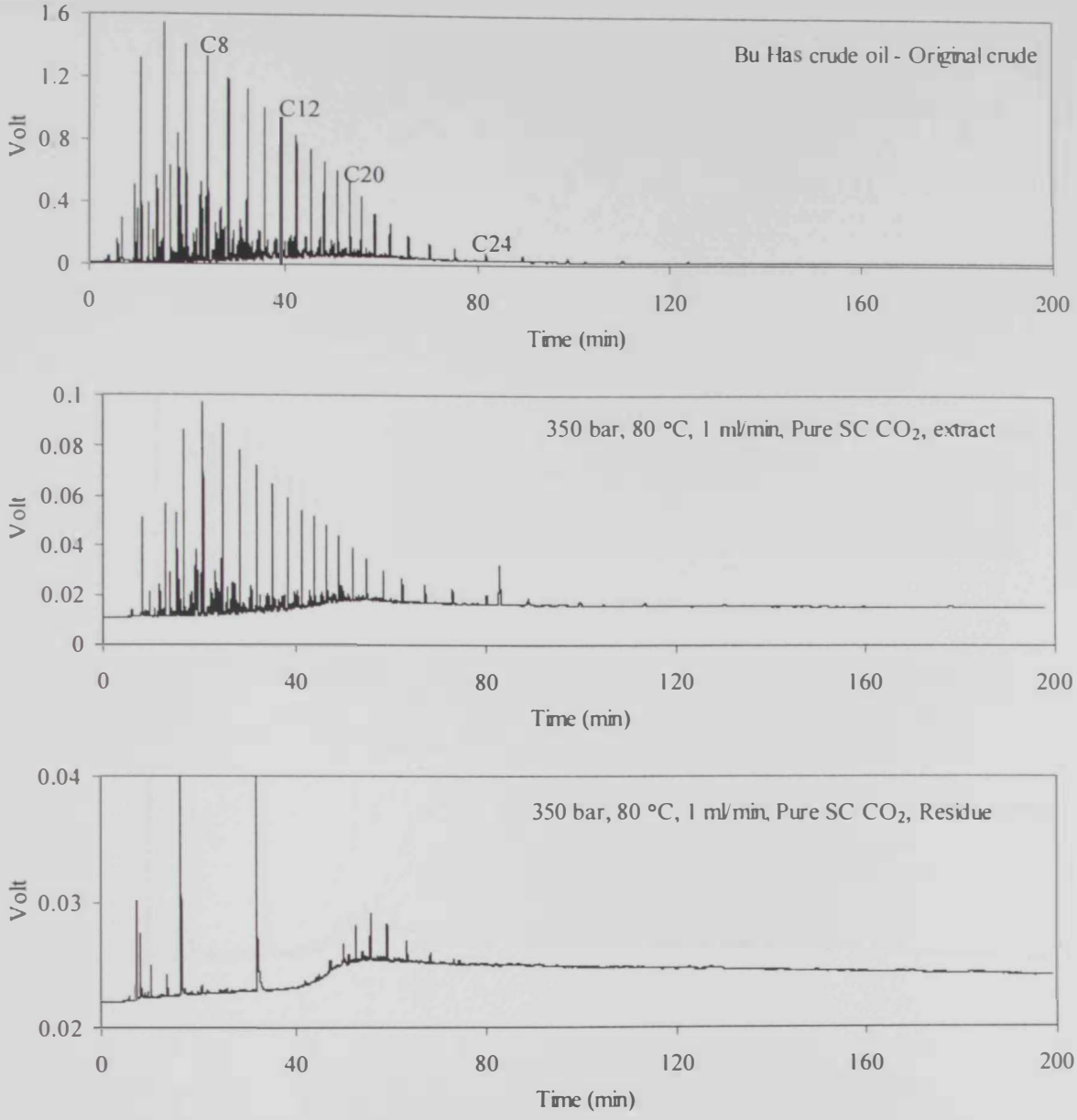


Figure 18: Gas chromatograms of the original Bu Hasa crude oil, extract obtained from SFE, and the residue. SFE conditions: 350 bar and 80 °C, pure SC CO_2.

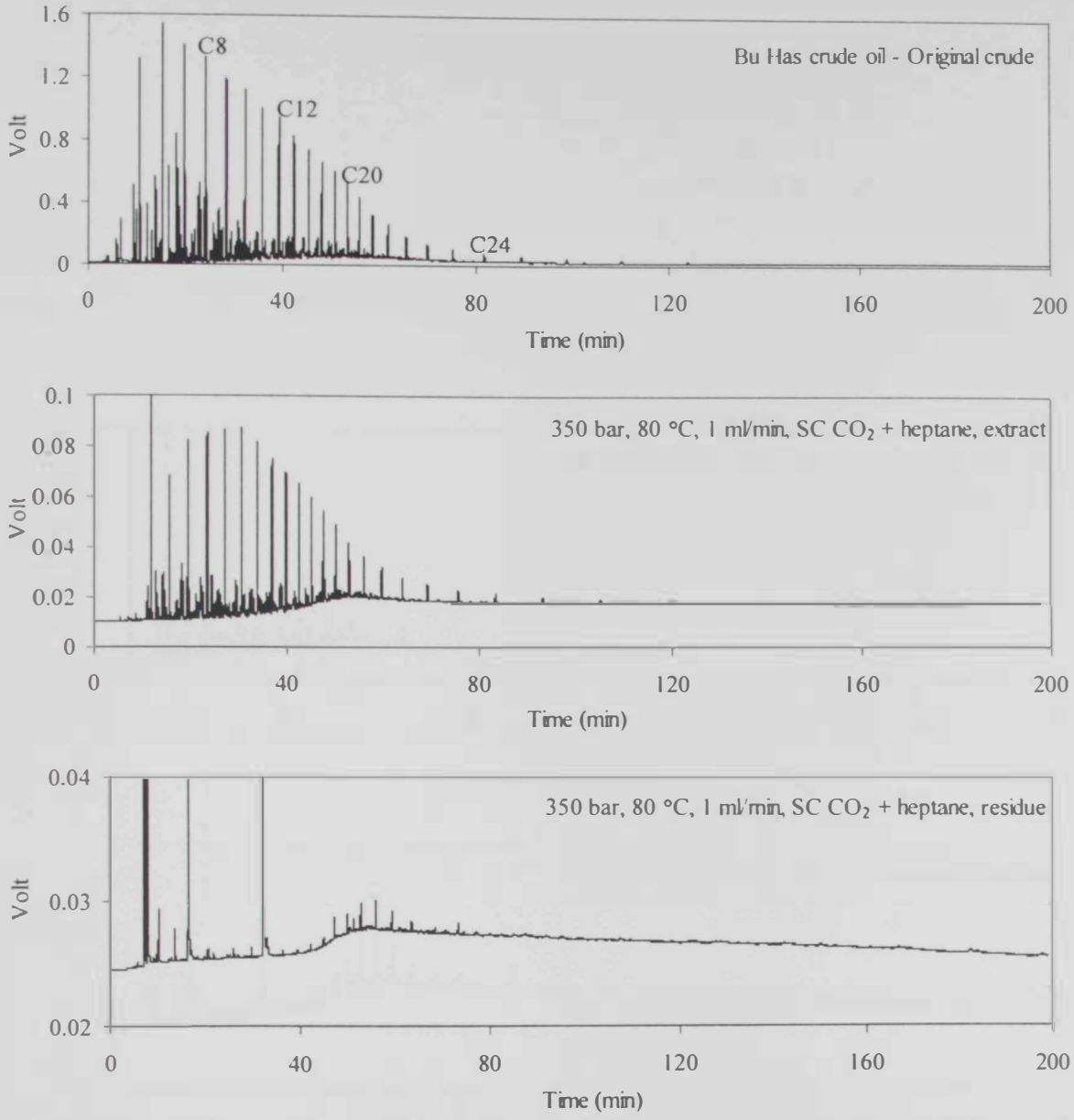


Figure 19: Gas chromatograms of the original Bu Hasa crude oil, extract obtained from SFE, and the residue. SFE conditions: 350 bar and 80 °C, SC CO_2 + 5% (v/v) heptane.

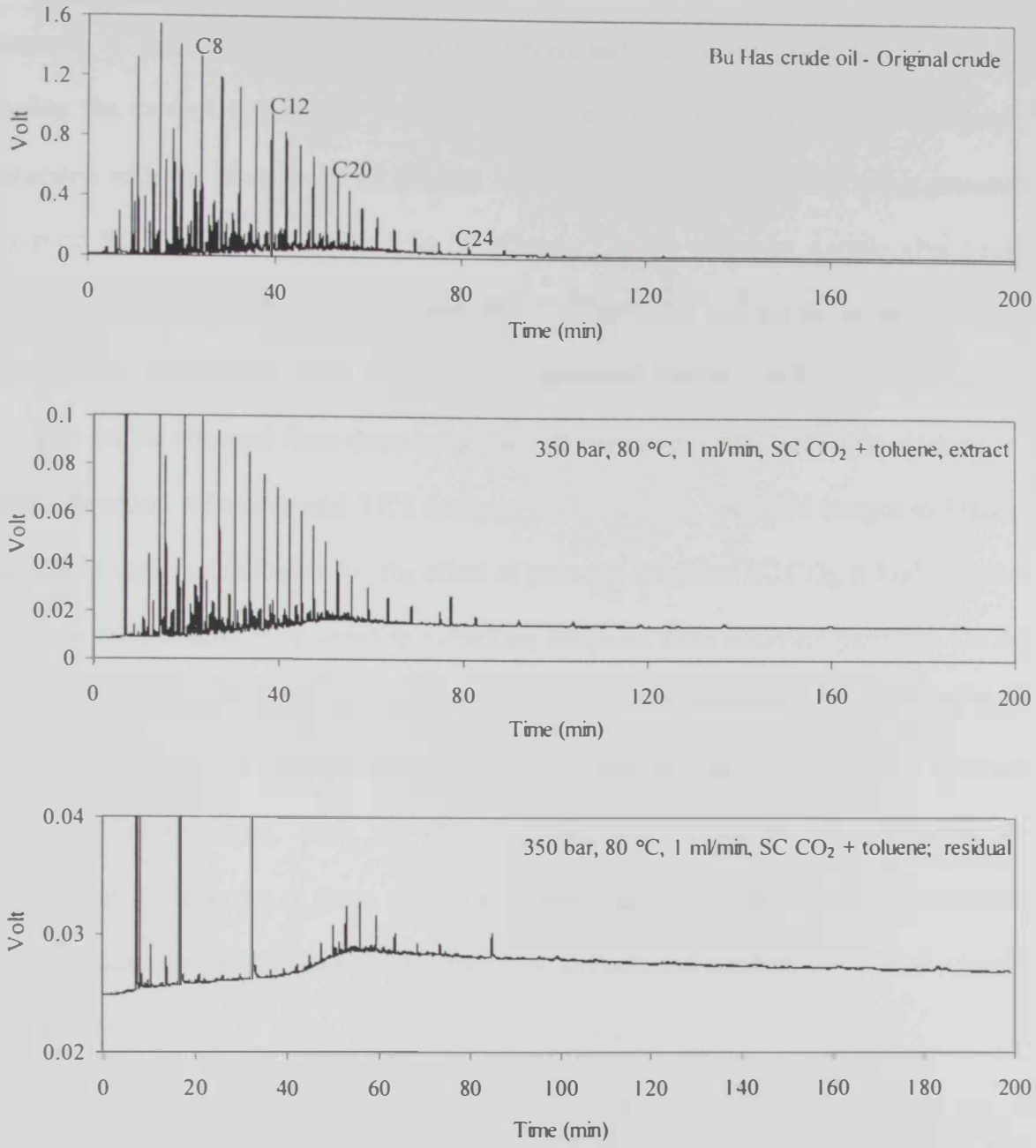


Figure 20: Gas chromatograms of the original Bu Hasa crude oil, extract obtained from SFE, and the residue. SFE conditions: 350 bar and 80 °C, SC CO_2 + 5% (v/v) toluene.

3.4.2. Scanning electron microscopy (SEM)

Scanning electron micrographs of selected sediment samples were used to study the capacity of the SC CO_2 to extract hydrocarbons and reduce the residual hydrocarbons during the extraction process. These micrographs are shown for the sediment sample saturated with Bu Hasa crude oil (Figure 21), for sediment sample after being extracted by pure SC CO_2 at 350 bar and 80 °C (Figure 22), for sediment sample after being extracted by pure SC CO_2 at 250 bar and 160 °C (Figure 23), and for the sediment sample extracted by modified SC CO2 with 5% (v/v) heptane at 350 bar and 80 °C (Figure 24).

The results obtained from these images are in agreement with the results obtained for both extraction efficiency and TPH analysis. By comparing the SEM images in Figures 22 and 24 with that in Figure 21, the effect of pure and modified SC CO_2, at high pressure and low temperature, is apparent in extracting crude oil from sediment particles. On the other hand, the SEM image of the pure SC CO_2 at low pressure (250 bar) and high temperature (160 °C) showed some remaining hydrocarbons or hydrocarbon residues (Figure 23). Therefore, pure SC CO_2 was not able to completely remediate the contaminated sediment at these conditions, which is in agreement with the previous observations obtained by the GC analysis of the extracts and residues and with the results in Table 6.

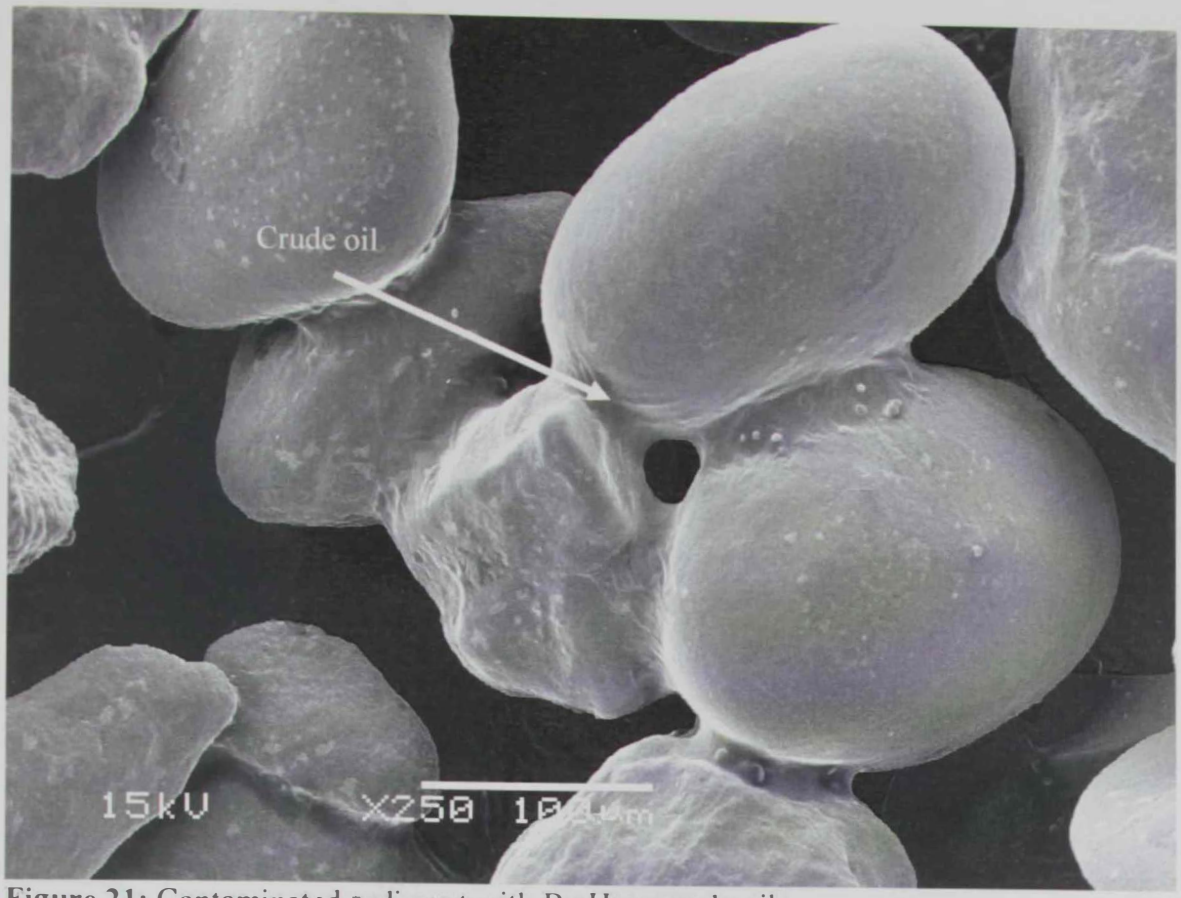


Figure 21: Contaminated sediment with Bu Hasa crude oil.

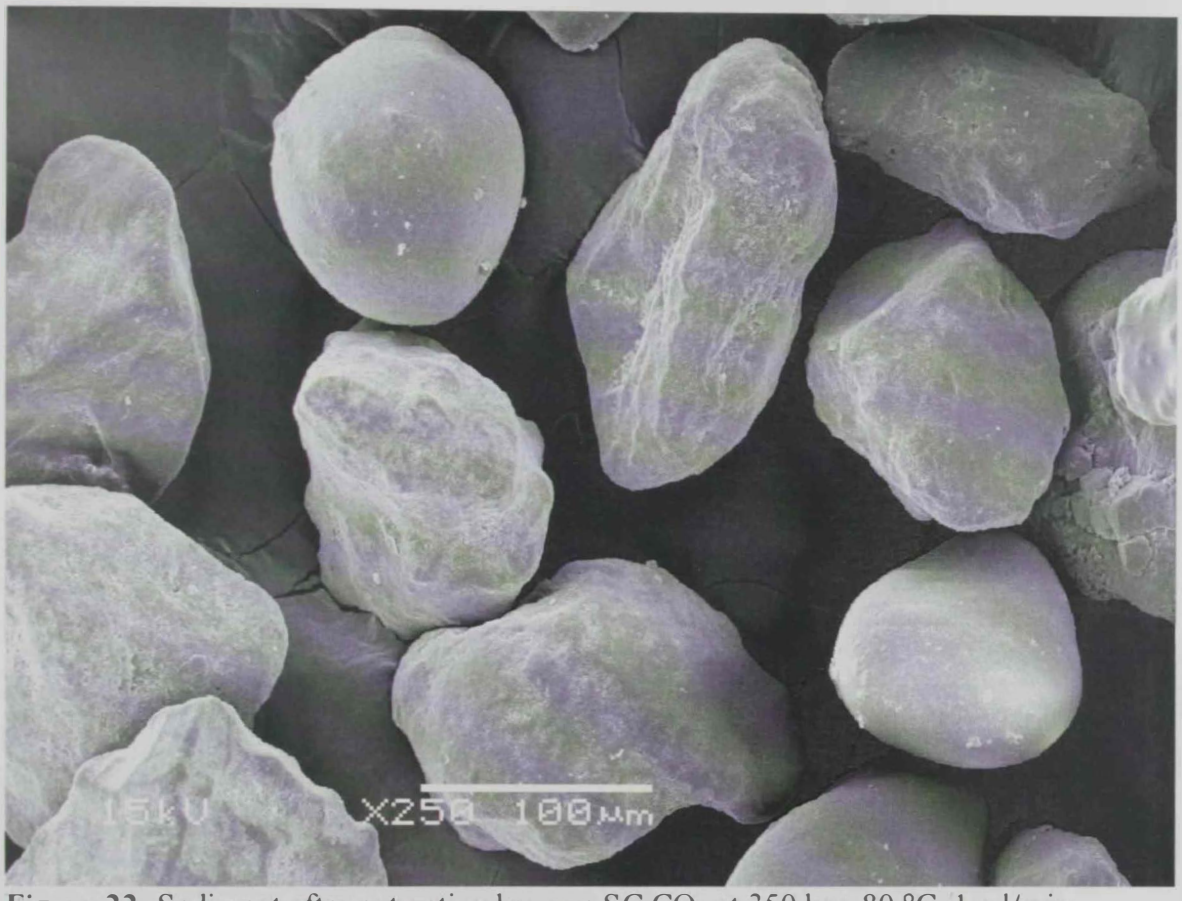


Figure 22: Sediment after extraction by pure SC CO_2 at 350 bar, 80 °C, 1 ml/min.

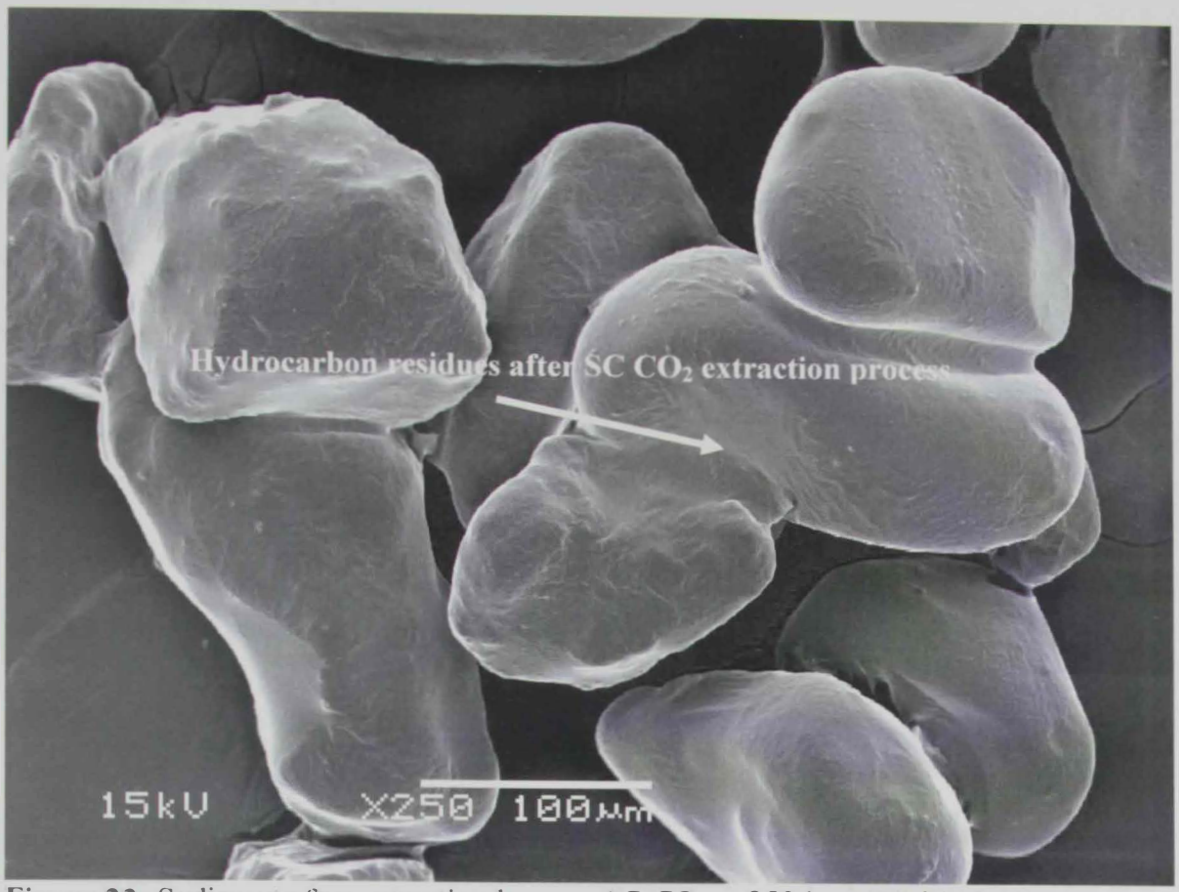


Figure 23: Sediment after extraction by pure SC CO_2 at 250 bar, 160 °C, 1 ml/min.

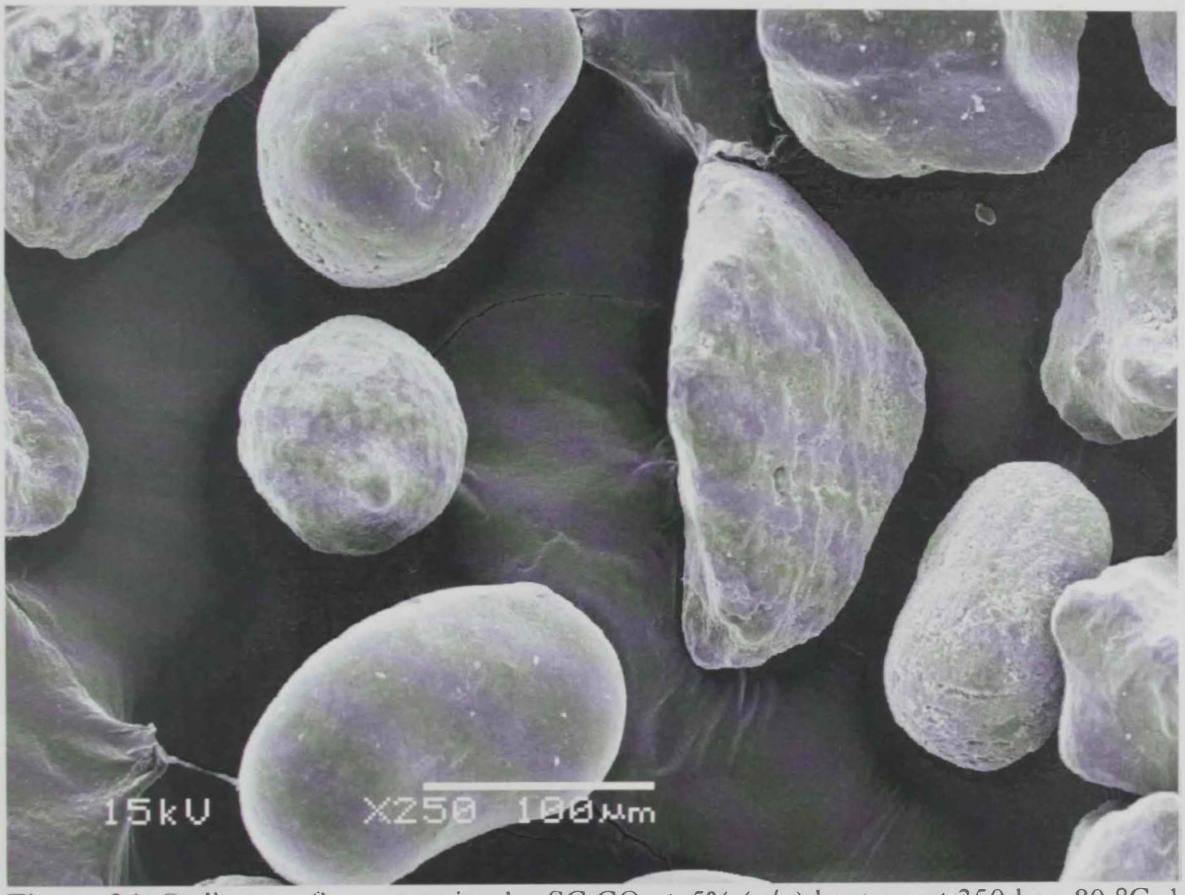


Figure 24: Sediment after extraction by SC CO_2 + 5% (v/v) heptane at 350 bar, 80 °C, 1 ml/min.

3.4.3. Total petroleum hydrocarbon (TPH) analysis

In this study, the capacity of SC CO_2 to extract TPH from sediment saturated with Bu Hasa crude oil was investigated for some selected runs. This study could show the best conditions to remediate the contaminated sediment and thus reduce the harmful effects of the TPH compounds on our health.

Based on Table 8, at high pressure (350 bar) and low temperature (80 °C), SC CO_2 is capable of extracting about 93% of TPH from the polluted sediment compared to about 76% removal of TPH at low pressure (250 bar) and high temperature (160 °C), which matches the results obtained from the extraction efficiency of SC CO_2 as shown in Table 6.

Table 8: TPH analysis of the clean sediment, oil-saturated sediment before SFE, and sediment samples after the SFE process.

		Temperature (°C)	Pressure (bar)	TPH (µg/mg)	TPH (%w/w)	TPH recovery efficiency (%)	Extraction Efficiency * (%)
Clean sediment	Blank	–	–	< 0.23	0.00	–	–
Sediment Sample before SFE	Crude oil	–	–	56875	5.69	–	–
Sediment samples after SFE	Run 15	80	350	4057	0.41	92.86	78.69
	Run 11	160	250	13564	1.36	76.15	69.22
	Run 13	160	350	5129	0.51	90.98	77.95
	Run 12	80	250	9361	0.94	83.54	71.83

*Extraction efficiency is for a single run, not an average of repeated runs.

3.4.4. Polycyclic Aromatic Hydrocarbon (PAH) analysis

In this study, the PAH measurement was conducted for selected runs to investigate the efficiency of SC CO_2 in extracting PAHs from sediment samples contaminated with Bu Hasa crude oil. The results for the concentration of 16 PAHs in the selected sediment samples after the SFE process are presented in Table 9.

Based on results shown in Table 9, the contaminated soil sample with Bu Hasa crude oil has low (undetectable) concentration of Acenaphthylene, Anthracene, Benzo(b)flouranthene, Benzo(k)flouranthene and Benzo(a)pyrene. Supercritical fluids used in this investigacation were able to significantly remove or reduce the concentration of Naphthalene, Acenaphthene, Flourene, Phenanthrene Fluoranthene, Pyrene, Benzo(a)anthracene, Chrycene, Dibenzo(a,h)anthracene, Benzo(g,h,i)perylene, Indeno(1,2,3-cd)pyrene).

Pure SC CO_2, at 160 °C and 350 bar, removed all PAH compounds with efficiency greatere than 98%. At all conditions, Naphthalene, Acenaphthene, Flourene, Benzo(a)anthracene, Chrycene, and Dibenzo(a,h)anthracene were removed with an efficiency greater than 99%.

The efficiency of SC CO_2 to remove Pyrene at all extraction conditions was low compared to other PAH compounds. However, extractions at 80 °C show lower efficiency to extract Pyrene and Phenanthrene than that at 160 °C. This might be attributed to the effect of high temperature, which increases the volatility of the PAHs and thus increases their solubility in the fluid. Further studies are needed to confirm this result.

Table 9: PAH analyses of the clean sediment, oil-saturated sediment before SFE and sediment samples after the SFE process. Removal efficiencies (%) are shown in parenthesis. Removal efficiency was assumed 100% for PAH concentration < LOD*.

Sample		Clean Sediment	Oil-contaminated sedimant before SFE	Oil-contaminated sediment samples after SFE				
				Run 15	Run 11	Run 13	Run 12	Run 20
Temperature (°C)		–	–	80	160	160	80	80
Pressure (bar)		–	–	350	250	350	250	350
Modifier		–	–	–	–	–	–	Heptane
PAH (µg/Kg)	Naphthalene	<7.89	10648	<7.89 (100%)	<7.89 (100%)	<7.89 (100%)	<7.89 (100%)	78 (99.26%)
	Acenaphthylene	<10.7	<10.7	<10.7	<10.7	<10.7	<10.7	<10.7
	Acenaphthene	<5.12	3260	7.89 (99.75%)	16.8 (99.48%)	15.4 (99.52%)	16 (99.50%)	19.5 (99.40%)
	Flourene	<5.53	357	<5.53 (100%)	<5.53 (100%)	<5.53 (100%)	<5.53 (100%)	<5.53 (100%)
	Phenanthrene	<4.85	10417	279 (97.32%)	66.8 (99.35%)	75.1 (99.27%)	553 94.69%)	292 (97.19%)
	Anthracene	<4.99	<4.99	<4.99	<4.99	<4.99	<4.99	<4.99
	Fluoranthene	<4.98	947	42.3 (95.53%)	32.3 (96.58%)	<4.98 (100%)	8.19 (99.13%)	40.2 (95.75%)
	Pyrene	<5.00	3921	924 (76.43%)	274 (93.01%)	63.1 (98.39%)	393 (89.97%)	622 (84.13%)
	Benzo(a)anthracene	<4.90	1168	<4.90 (100%)	9.53 (99.18%)	11.4 (99.02%)	<4.90 (100%)	9.85 (99.15%)
	Chrycene	<4.92	1107	9.85 (99.11%)	<4.92 (100%)	10.3 (99.06%)	<4.92 (100%)	10.8 (99.02%)
	Benzo(b)flouranthene	<4.54	<4.54	<4.54	<4.54	<4.54	<4.54	<4.54
	Benzo(k)flouranthene	<4.61	<4.61	<4.61	<4.61	<4.61	<4.61	<4.61
	Benzo(a)pyrene	<4.99	<4.99	<4.99	<4.99	<4.99	<4.99	<4.99
	Dibenzo(a,h)anthracene	<5.34	283	<5.34 (100%)	<5.34 (100%)	<5.34 (100%)	<5.34 (100%)	<5.34 (100%)
	Benzo(g,h,i)perylene	<5.45	750	37 (95.06%)	<5.45 (100%)	<5.45 (100%)	<5.45 (100%)	13.8 (98.16%)
	Indeno(1,2,3-cd)pyrene	<5.42	326	36.2 (88.89%)	<5.42 (100%)	<5.42 (100%)	<5.42 (100%)	<5.42 (100%)
Extraction efficiency (%)**		–	–	**78.69**	**69.22**	**77.95**	**71.83**	**97.66**

* LOD: limit of detection.

** Extraction efficiency is for a single run, not an average of repeated runs.

CHAPTER 4

CONCLUSIONS

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Effects of temperature, pressure, CO_2 flow rate and modifier type added as 5% (v/v) on the extraction capacity of SC CO_2 from contaminated sediment have been investigated in this study. The results of this study indicated that SC CO_2 is an effective solvent, which lead to higher oil recoveries when applied at the high pressure (350) bar. Furthermore, the results show that the investigated flow rates do not have a significant effect on the efficiency of SC CO_2 to extract hydrocarbons from contaminated sediment. Therefore, it is recommended to use the high flow rate, i.e. 4 ml/min, in order to reduce the time required for the remediation of contaminated sediments. Moreover, the temperature, i.e. 80 and 160 °C, has no significant effect on the extraction efficiency of SC CO_2 at the high pressure (350 bar). Therefore, it is recommended to apply the low temperature during the extraction process in order to save energy. Additionally, for sediments contaminated by Bu Hasa crude oil, chemical modification of CO_2 by adding 5% (v/v) heptane is more effective than adding 5% (v/v) toluene.

The best conditions to extract up to (92.26 %) of the hydrocarbons in the sediments contaminated with Bu Hasa crude oil was by the modified SC CO_2 with 5% (v/v) heptane at high pressure (350 bar), low temperature (80 °C), and flow rate of 1 ml/min. However, pure SC CO_2 was able to extract up to 77 % of the crude oil in the sediment at the same conditions. Therefore, it is suggested to utilize pure CO_2 at these conditions to extract the hydrocarbons from contaminated sediments in order to avoid the harmful impact of the organic solvent on the environment.

Supercritical CO_2 at high pressure (350 bar) and low temperature (80 °C) is an effective remediation technique, which minimizes the residual hydrocarbons as shown on the GC chromatograms and SEM images. Moreover, pure SC CO_2 was able to remove

more than 93% of the TPHs present in sediment contaminated by Bu Hasa crude oil. Furthermore, pure SC CO_2 and SC CO_2 chemically modified with 5% (v/v) heptane were capable of reducing the concentration levels of PAHs in the contaminated sediments by Bu Hasa crude oil.

Additionally, in this study, the effect of particle type (sediment and limestone) and size on the SC CO_2 extraction capacity at reservoir conditions was investigated. The results show that extraction efficiency of CO_2 from sediment (71.14%) is higher than that from limestone particles (61.02%) of the same size and distribution, indicating that Bu Hasa oil holds more strongly to the limestone particles than to the sediment particles. This is due to the differences in the physico-chemical properties of the limestone and sediment samples. Additionally, extraction efficiency was lower for the small limestone particles, which is attributed to its larger surface area compared to that of larger particles.

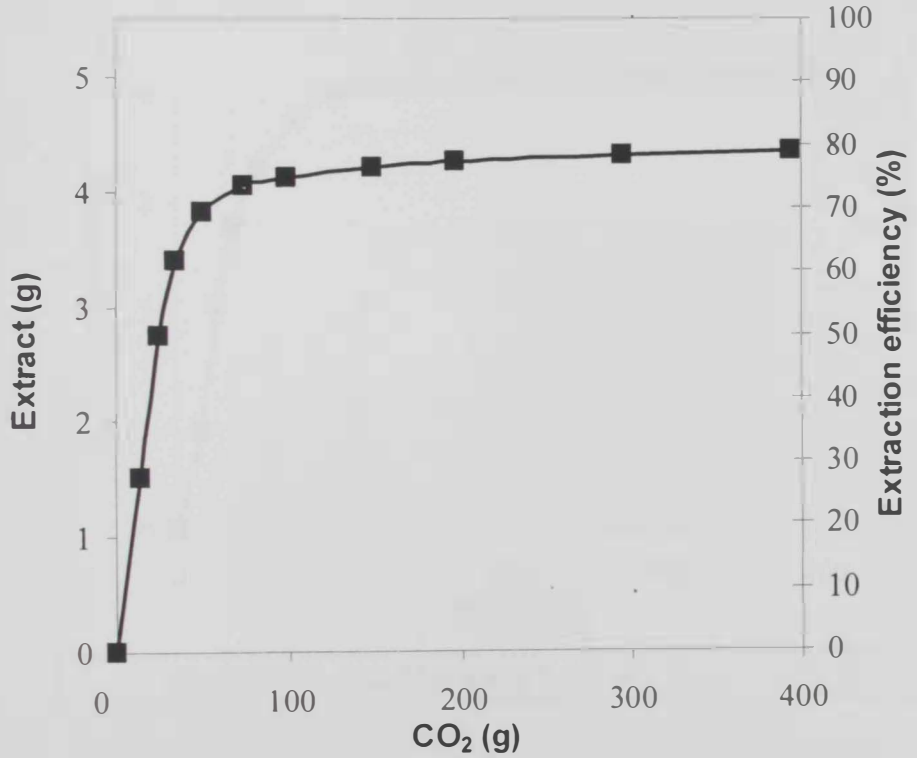
APPENDICES

Appendix I: SFE experimental results

SFE experimental results for pure CO_2

Run Number: 1

Conditions					
Temperature (°C)	Pressure (bar)	Flow Rate (ml/min)		Fluid Type	
80	350	4		CO_2 Only	
CO_2 Density (g) =	0.98661			Initial oil mass (g) =	5.5111
				Sample weight (g) =	60.62
CO_2 Volume (ml)	CO_2 Mass (g)	Extract weight (g)		Efficiency (%)	
		cumulative	absolute	cumulative	absolute
0	0.00	0.00	0.00	0.00	0.00
15	14.80	1.52	1.52	27.54	27.54
25	24.67	2.74	1.22	49.71	22.16
35	34.53	3.40	0.66	61.66	11.95
50	49.33	3.83	0.43	69.42	7.76
75	74.00	4.04	0.22	73.38	3.96
100	98.66	4.13	0.08	74.90	1.52
150	147.99	4.21	0.08	76.34	1.44
200	197.32	4.26	0.05	77.27	0.93
300	295.98	4.32	0.06	78.36	1.09
400	394.64	4.35	0.03	78.87	0.51

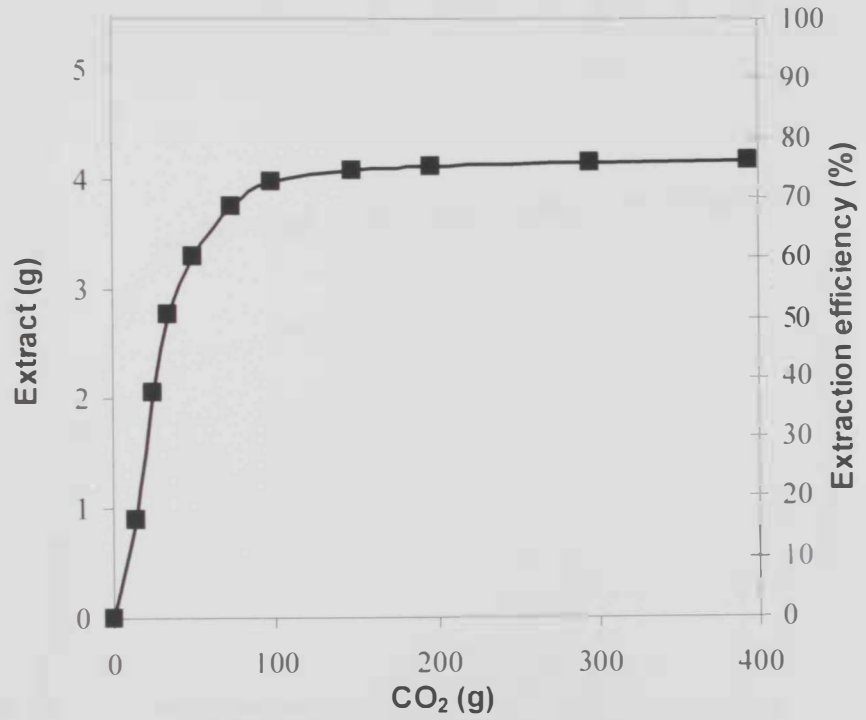


Final Extraction Efficiency % =	78.87

Run Number: 2

Conditions			
Temperature (°C)	Pressure (bar)	Flow Rate (ml/min)	Fluid Type
80	350	4	CO_2 Only
CO_2 Density (g) =	0.98661	Initial oil mass (g) =	5.4797
		Sample weight (g) =	60.31

CO_2 Volume (ml)	CO_2 Mass (g)	Extract weight (g)		Efficiency (%)	
		cumulative	absolute	cumulative	absolute
0	0.00	0.00	0.00	0.00	0.00
15	14.80	0.90	0.90	16.40	16.40
25	24.67	2.04	1.14	37.24	20.84
35	34.53	2.76	0.72	50.46	13.21
50	49.33	3.30	0.53	60.14	9.68
75	74.00	3.75	0.46	68.49	8.35
100	98.66	3.98	0.23	72.60	4.11
150	147.99	4.07	0.10	74.34	1.74
200	197.32	4.11	0.04	75.02	0.69
300	295.98	4.14	0.03	75.59	0.57
400	394.64	4.16	0.02	75.92	0.34

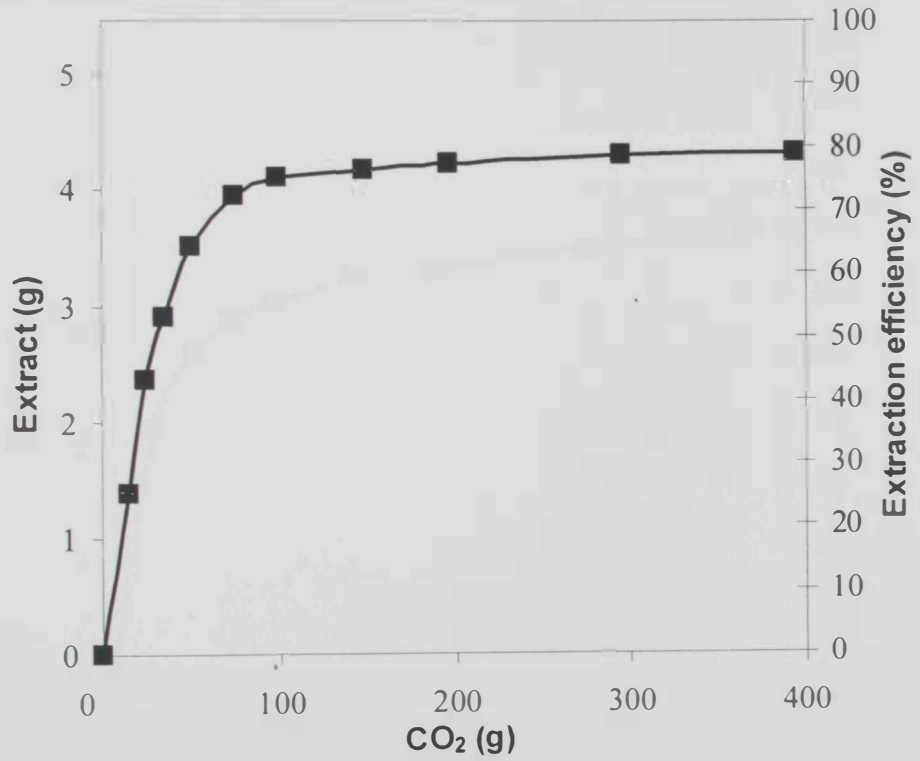


Final Extraction Efficiency % =	75.92

Run Number: 3

Conditions			
Temperature (°C)	Pressure (bar)	Flow Rate (ml/min)	Fluid Type
160	350	1	Pure CO_2
CO_2 Density (g) = 0.98661			Initial oil mass (g) = 5.4770 Sample weight (g) = 60.27

CO_2 Volume (ml)	CO_2 Mass (g)	Extract weight (g)		Efficiency (%)	
		cumulative	absolute	cumulative	absolute
0	0.00	0.00	0.00	0.00	0.00
15	14.80	1.37	1.37	25.10	25.10
25	24.67	2.36	0.98	43.07	17.97
35	34.53	2.90	0.54	52.89	9.83
50	49.33	3.51	0.62	64.14	11.25
75	74.00	3.95	0.43	72.06	7.92
100	98.66	4.12	0.17	75.23	3.17
150	147.99	4.18	0.06	76.29	1.06
200	197.32	4.24	0.06	77.40	1.11
300	295.98	4.30	0.06	78.49	1.09
400	394.64	4.33	0.03	79.06	0.57

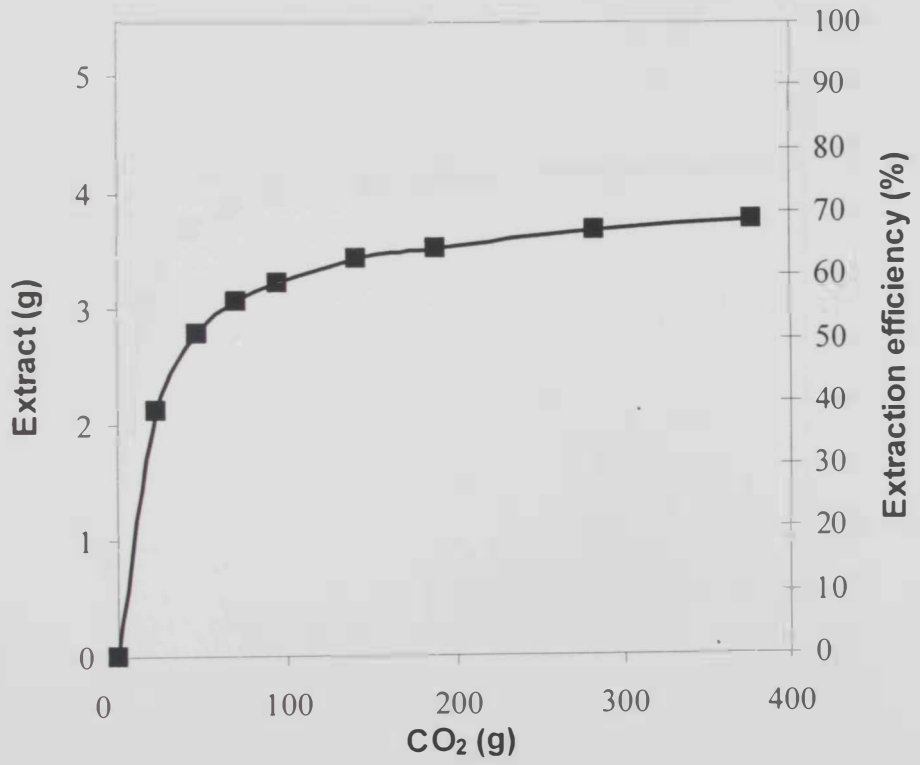


Final Extraction Efficiency % =	79.06

Run Number: 4

Conditions			
Temperature (°C)	Pressure (bar)	Flow Rate (ml/min)	Fluid Type
160	250	4	Pure CO_2
CO2 Density (g) =	0.94298	Initial oil mass (g) =	5.4803
		Sample weight (g) =	60.26

CO_2 Volume (ml)	CO_2 Mass (g)	Extract weight (g)		Efficiency (%)	
		cumulative	absolute	cumulative	absolute
0	0.00	0.00	0.00	0.00	0.00
25	23.57	2.13	2.13	38.78	38.78
50	47.15	2.78	0.66	50.79	12.01
75	70.72	3.06	0.28	55.85	5.05
100	94.30	3.22	0.16	58.79	2.94
150	141.45	3.43	0.21	62.55	3.76
200	188.60	3.53	0.10	64.34	1.80
300	282.89	3.68	0.15	67.17	2.82
400	377.19	3.76	0.08	68.57	1.40

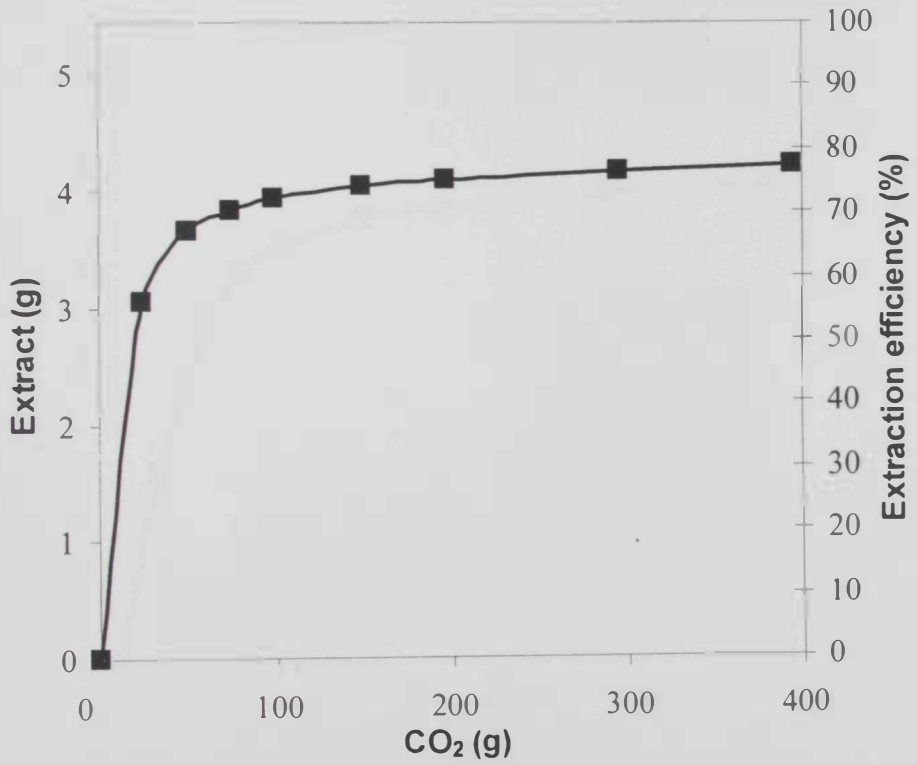


Final Extraction Efficiency % =	68.57

Run Number: 5

Conditions			
Temperature (°C)	Pressure (bar)	Flow Rate (ml/min)	Fluid Type
160	350	4	Pure CO_2
CO2 Density (g) =	0.98661	Initial oil mass (g) =	5.4560
		Sample weight (g) =	59.98

CO_2 Volume (ml)	CO_2 Mass (g)	Extract weight (g)		Efficiency (%)	
		cumulative	absolute	cumulative	absolute
0	0.00	0.00	0.00	0.00	0.00
25	24.67	3.05	3.05	55.99	55.99
50	49.33	3.66	0.61	67.14	11.15
75	74.00	3.84	0.18	70.40	3.26
100	98.66	3.94	0.10	72.21	1.81
150	147.99	4.04	0.10	74.10	1.89
200	197.32	4.10	0.06	75.19	1.09
300	295.98	4.17	0.07	76.50	1.31
400	394.64	4.23	0.06	77.54	1.04

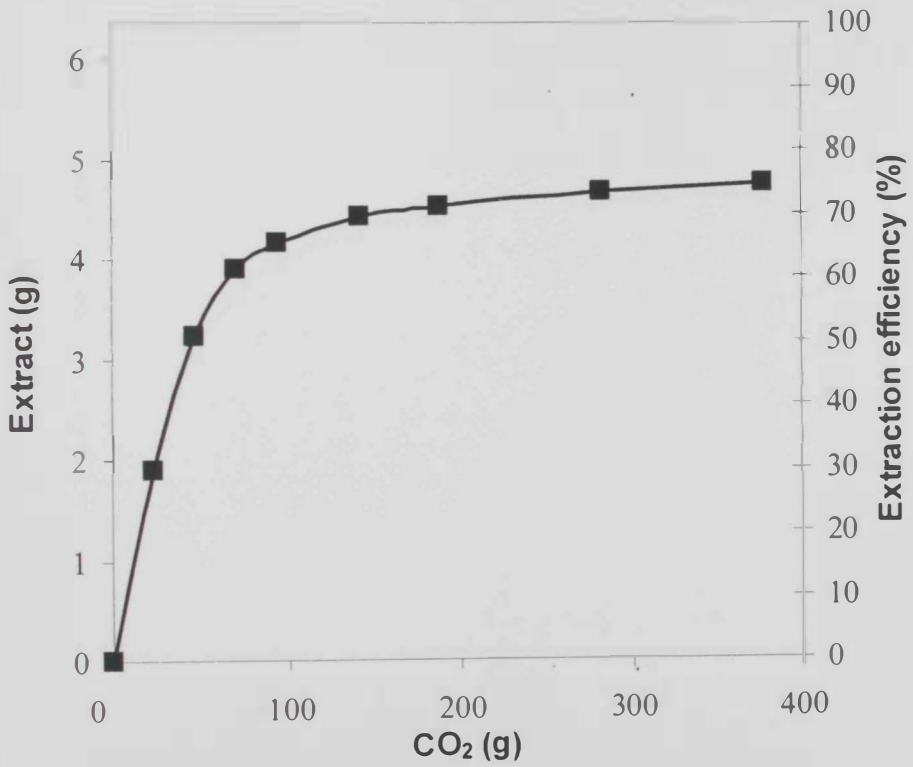


Final Extraction Efficiency % =	77.54

Run Number: 6

Conditions			
Temperature (°C)	Pressure (bar)	Flow Rate (ml/min)	Fluid Type
80	250	4	Pure CO_2
CO_2 Density (g) = 0.94298		Initial oil mass (g) = 6.3697	
		Sample weight (g) = 70.09	

CO_2 Volume (ml)	CO_2 Mass (g)	Extract weight (g)		Efficiency (%)	
		cumulative	absolute	cumulative	absolute
0	0.00	0.00	0.00	0.00	0.00
25	23.57	1.90	1.90	29.84	29.84
50	47.15	3.23	1.33	50.68	20.84
75	70.72	3.90	0.67	61.18	10.50
100	94.30	4.17	0.27	65.47	4.29
150	141.45	4.42	0.25	69.46	3.98
200	188.60	4.52	0.10	71.02	1.56
300	282.89	4.68	0.15	73.44	2.43
400	377.19	4.75	0.08	74.64	1.20

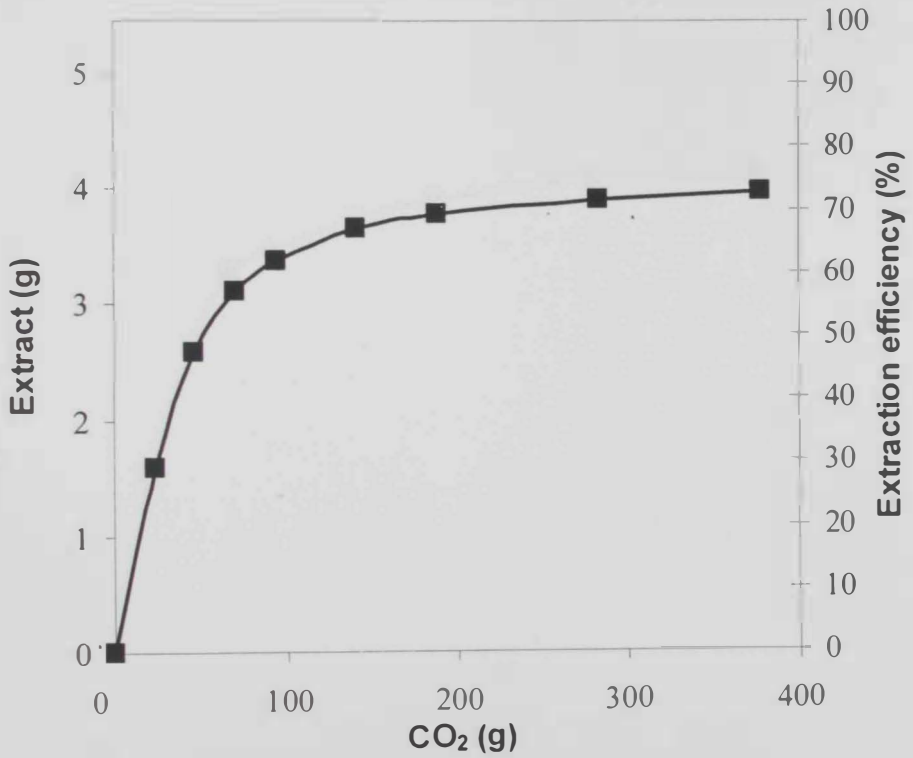


Final Extraction Efficiency % =	74.64

Run Number: 7

Conditions			
Temperature (°C)	Pressure (bar)	Flow Rate (ml/min)	Fluid Type
80	250	1	Pure CO_2
CO_2 Density (g) = 0.94298		Initial oil mass (g) = 5.4572	
		Sample weight (g) = 60.14	

CO_2 Volume (ml)	CO_2 Mass (g)	Extract weight (g)		Efficiency (%)	
		cumulative	absolute	cumulative	absolute
0	0.00	0.00	0.00	0.00	0.00
25	23.57	1.59	1.59	29.15	29.15
50	47.15	2.58	0.99	47.32	18.17
75	70.72	3.12	0.53	57.10	9.77
100	94.30	3.38	0.27	61.96	4.86
150	141.45	3.65	0.27	66.88	4.92
200	188.60	3.78	0.13	69.23	2.35
300	282.89	3.91	0.13	71.56	2.33
400	377.19	3.97	0.07	72.81	1.25

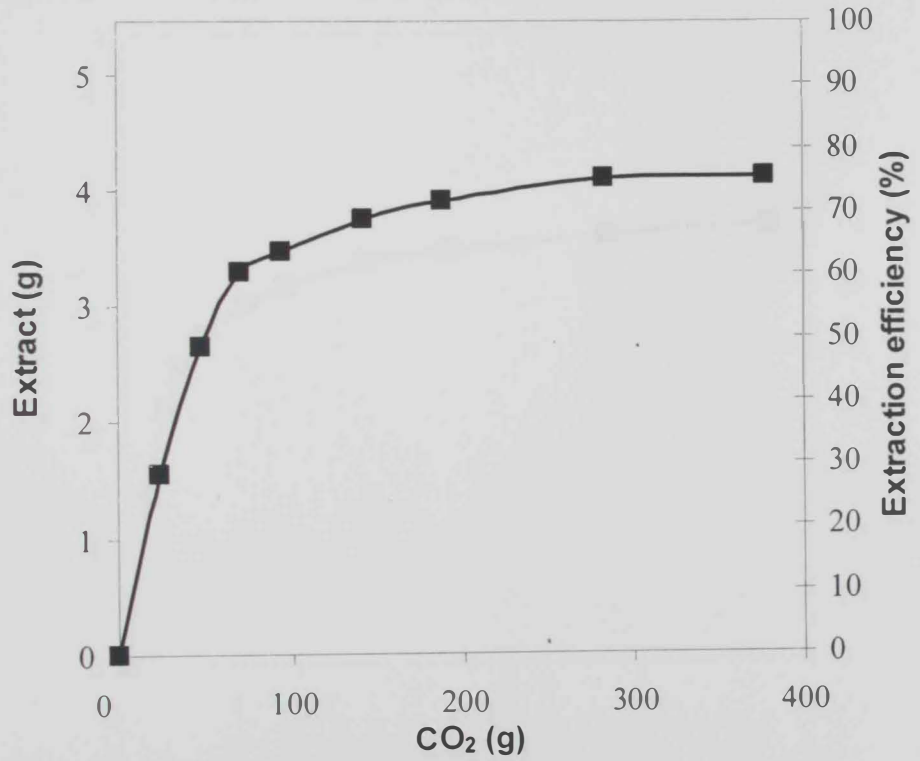


Final Extraction Efficiency % =	72.81

Run Number: 8

Conditions			
Temperature (°C)	Pressure (bar)	Flow Rate (ml/min)	Fluid Type
80	250	4	CO_2 Only
CO_2 Density (g) = 0.94298		Initial oil mass (g) = 5.4645	
		Sample weight (g) = 60.05	

CO_2 Volume (ml)	CO_2 Mass (g)	Extract weight (g)		Efficiency (%)	
		cumulative	absolute	cumulative	absolute
0	0.00	0.00	0.00	0.00	0.00
25	23.57	1.55	1.55	28.44	28.44
50	47.15	2.66	1.11	48.70	20.26
75	70.72	3.30	0.63	60.32	11.62
100	94.30	3.48	0.18	63.69	3.37
150	141.45	3.76	0.28	68.79	5.09
200	188.60	3.90	0.14	71.44	2.65
300	282.89	4.11	0.21	75.20	3.76
400	377.19	4.13	0.02	75.50	0.30

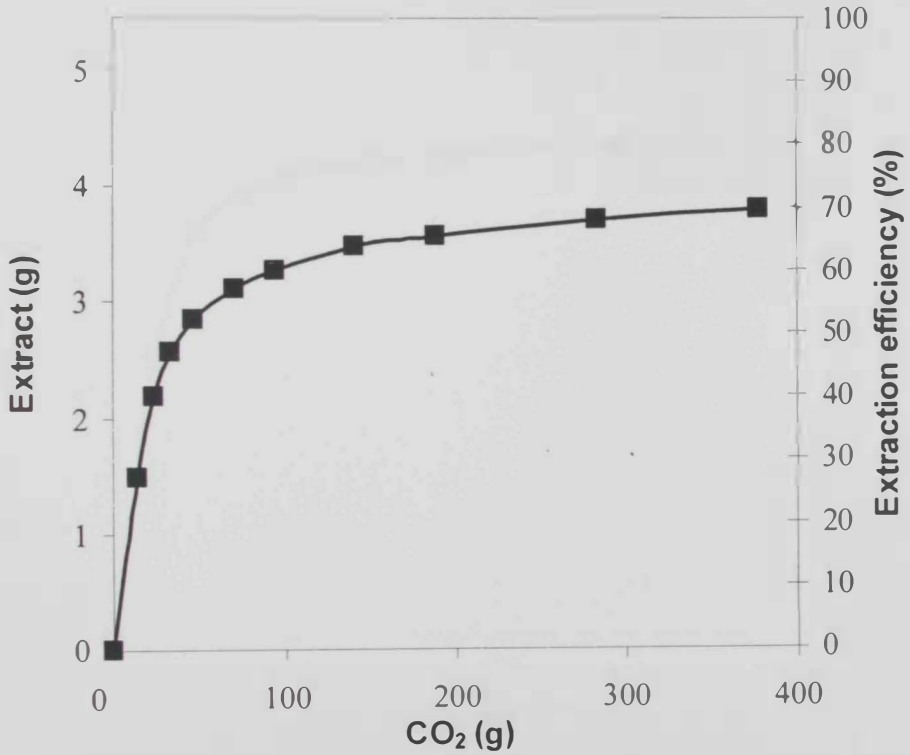


Final Extraction Efficiency % =	75.50

Run Number: 9

Conditions			
Temperature (°C)	Pressure (bar)	Flow Rate (ml/min)	Fluid Type
160	250	4	Pure CO_2
CO_2 Density (g) =	0.94298	Initial oil mass (g) =	5.4562
		Sample weight (g) =	60.01

CO_2 Volume (ml)	CO_2 Mass (g)	Extract weight (g)		Efficiency (%)	
		cumulative	absolute	cumulative	absolute
0	0.00	0.00	0.00	0.00	0.00
15	14.14	1.48	1.48	27.12	27.12
25	23.57	2.18	2.18	39.98	12.86
35	33.00	2.56	0.38	46.98	7.00
50	47.15	2.85	0.67	52.23	5.25
75	70.72	3.10	0.25	56.89	4.66
100	94.30	3.27	0.16	59.84	2.95
150	141.45	3.47	0.21	63.63	3.79
200	188.60	3.57	0.10	65.51	1.88
300	282.89	3.70	0.13	67.82	2.31
400	377.19	3.79	0.09	69.49	1.68

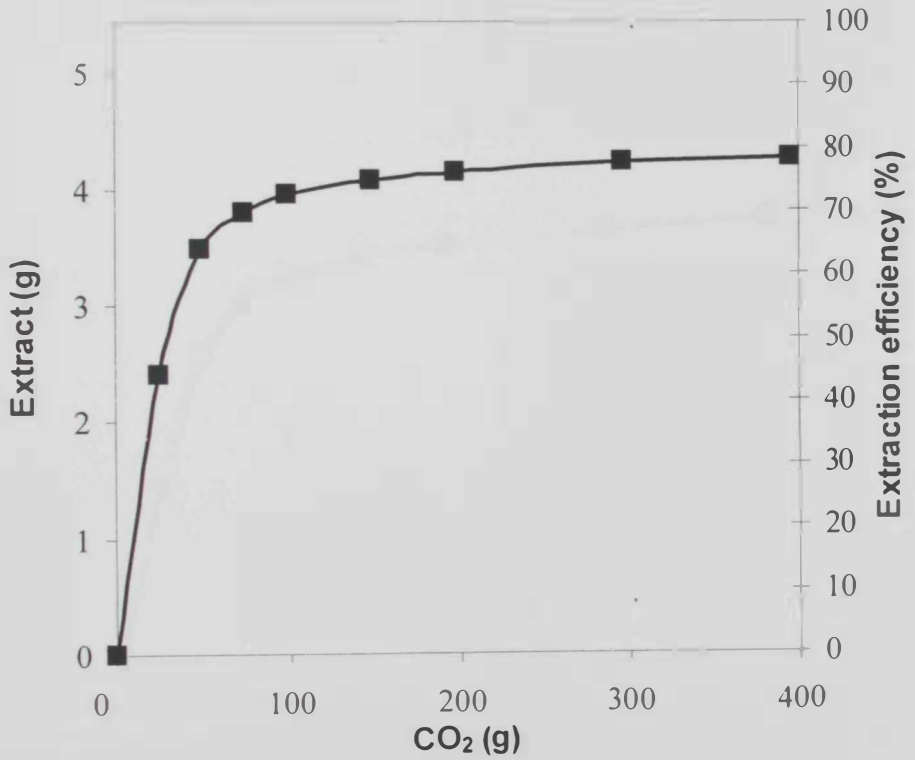


Final Extraction Efficiency % =	69.49

Run Number: 10

Conditions			
Temperature (°C)	Pressure (bar)	Flow Rate (ml/min)	Fluid Type
160	350	4	Pure CO_2
CO_2 Density (g) =	0.98661	Initial oil mass (g) =	5.4589
		Sample weight (g) =	60.01

CO_2 Volume (ml)	CO_2 Mass (g)	Extract weight (g)		Efficiency (%)	
		cumulative	absolute	cumulative	absolute
0	0.00	0.00	0.00	0.00	0.00
25	24.67	2.40	2.40	43.95	43.95
50	49.33	3.49	1.09	63.85	19.90
75	74.00	3.80	0.31	69.53	5.68
100	98.66	3.96	0.17	72.56	3.02
150	147.99	4.08	0.12	74.79	2.23
200	197.32	4.14	0.06	75.93	1.14
300	295.98	4.24	0.09	77.66	1.73
400	394.64	4.27	0.03	78.28	0.62

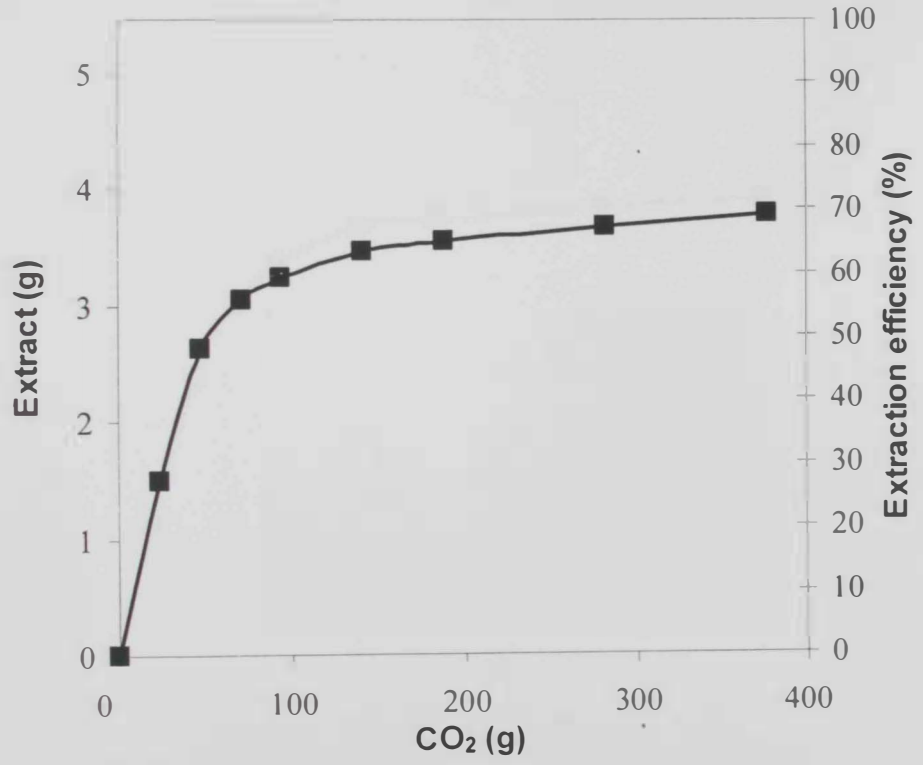


Final Extraction Efficiency % =	78.28

Run Number: 11

Conditions			
Temperature (°C)	Pressure (bar)	Flow Rate (ml/min)	Fluid Type
160	250	1	Pure CO_2
CO_2 Density (g) = 0.94298		Initial oil mass (g) = 5.4628	
		Sample weight (g) = 60.07	

CO_2 Volume (ml)	CO_2 Mass (g)	Extract weight (g)		Efficiency (%)	
		cumulative	absolute	cumulative	absolute
0	0.00	0.00	0.00	0.00	0.00
25	23.57	1.50	1.50	27.52	27.52
50	47.15	2.62	1.12	47.98	20.45
75	70.72	3.05	0.43	55.86	7.88
100	94.30	3.23	0.18	59.21	3.35
150	141.45	3.46	0.22	63.31	4.10
200	188.60	3.55	0.09	65.04	1.73
300	282.89	3.67	0.11	67.13	2.10
400	377.19	3.78	0.11	69.22	2.08

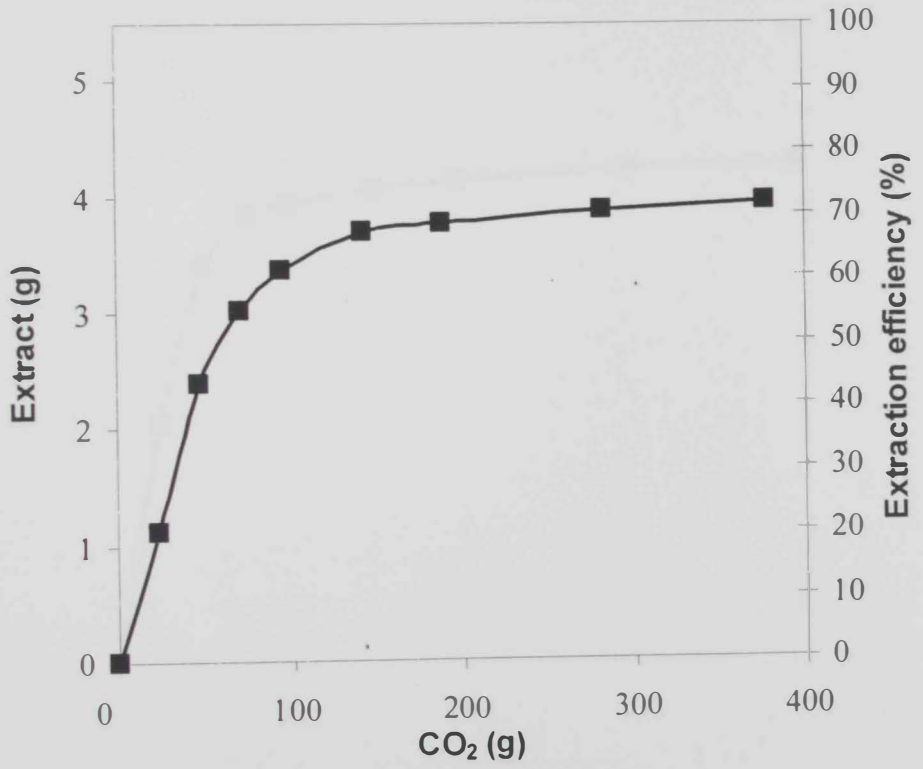


Final Extraction Efficiency % =	69.22

Run Number: 12

Conditions			
Temperature (°C)	Pressure (bar)	Flow Rate (ml/min)	Fluid Type
80	250	1	CO_2 Only
CO_2 Density (g) =	0.94298	Initial oil mass (g) =	5.4919
		Sample weight (g) =	60.43

CO_2 Volume (ml)	CO_2 Mass (g)	Extract weight (g)		Efficiency (%)	
		cumulative	absolute	cumulative	absolute
0	0.00	0.00	0.00	0.00	0.00
25	23.57	1.12	1.12	20.36	20.36
50	47.15	2.38	1.26	43.34	22.98
75	70.72	3.02	0.64	54.98	11.64
100	94.30	3.36	0.34	61.19	6.21
150	141.45	3.70	0.34	67.31	6.12
200	188.60	3.76	0.07	68.53	1.22
300	282.89	3.87	0.11	70.45	1.91
400	377.19	3.94	0.08	71.83	1.38

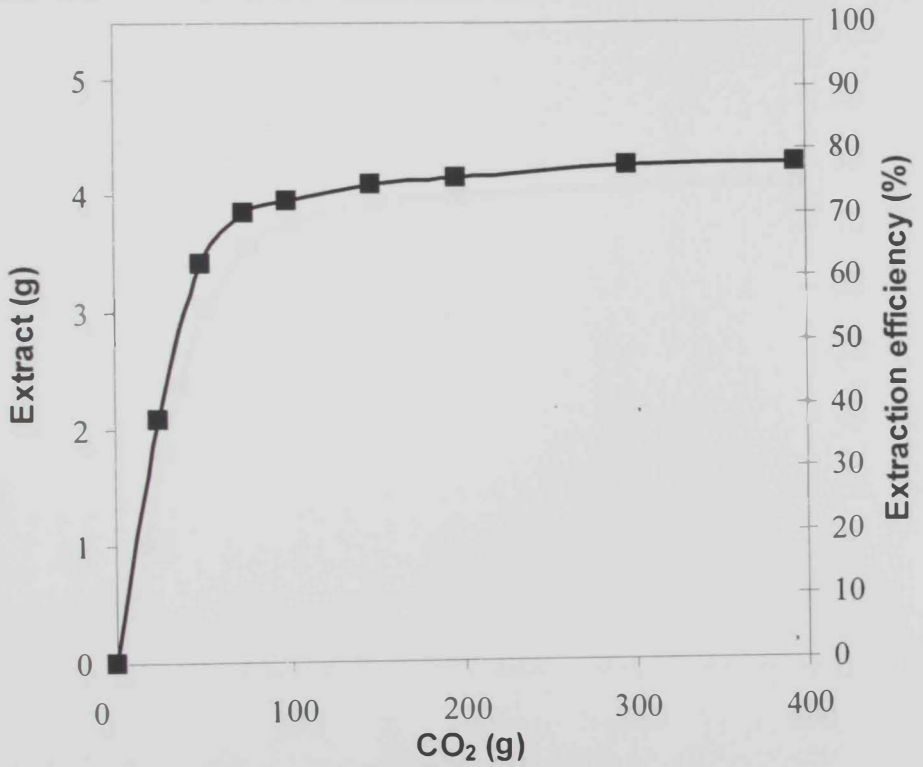


Final Extraction Efficiency % =	71.83

Run Number: 13

Conditions			
Temperature (°C)	Pressure (bar)	Flow Rate (ml/min)	Fluid Type
160	350	1	Pure CO_2
CO_2 Density (g) = 0.98661		Initial oil mass (g) = 5.4823	
		Sample weight (g) = 60.31	

CO_2 Volume (ml)	CO_2 Mass (g)	Extract weight (g)		Efficiency (%)	
		cumulative	absolute	cumulative	absolute
0	0.00	0.00	0.00	0.00	0.00
25	24.67	2.09	2.09	38.05	38.05
50	49.33	3.43	1.34	62.49	24.44
75	74.00	3.84	0.42	70.11	7.62
100	98.66	3.96	0.11	72.15	2.04
150	147.99	4.09	0.14	74.67	2.51
200	197.32	4.15	0.06	75.73	1.06
300	295.98	4.26	0.10	77.63	1.90
400	394.64	4.27	0.02	77.95	0.32

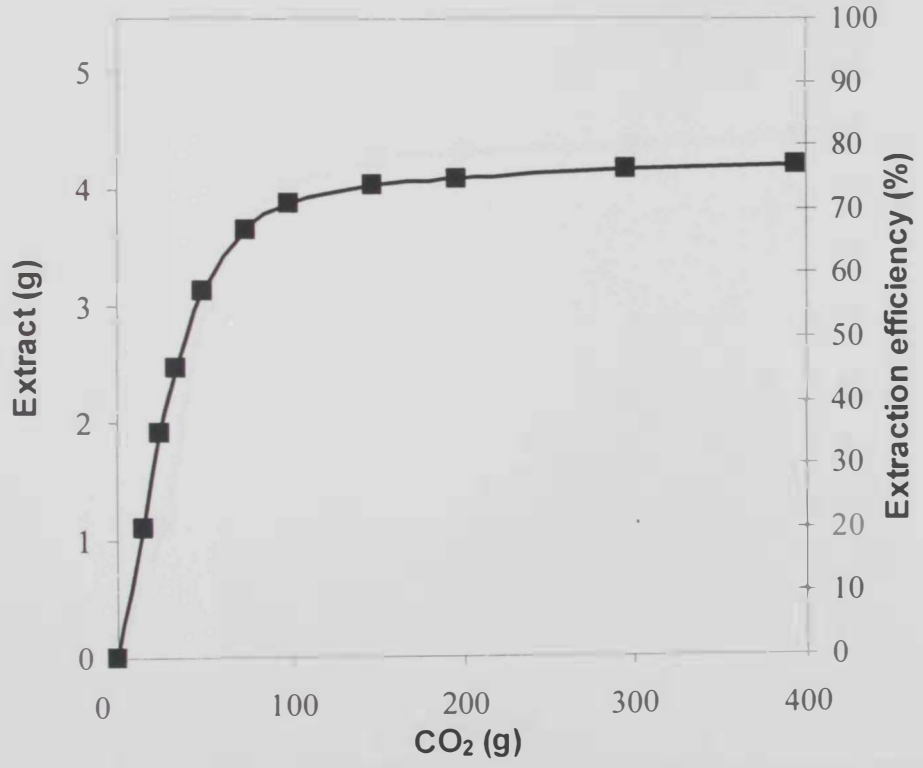


Final Extraction Efficiency % =	77.95

Run Number: 14

Conditions			
Temperature (°C)	Pressure (bar)	Flow Rate (ml/min)	Fluid Type
80	350	1	Pure CO_2
CO_2 Density (g) =	0.98661	Initial oil mass (g) =	5.4675
		Sample weight (g) =	60.17

CO_2 Volume (ml)	CO_2 Mass (g)	Extract weight (g)		Efficiency (%)	
		cumulative	absolute	cumulative	absolute
0	0.00	0.00	0.00	0.00	0.00
15	14.80	1.10	1.10	20.18	20.18
25	24.67	1.93	0.82	35.22	15.04
35	34.53	2.48	0.56	45.38	10.16
50	49.33	3.14	0.66	57.41	12.03
75	74.00	3.66	0.52	66.89	9.49
100	98.66	3.88	0.22	70.94	4.05
150	147.99	4.03	0.15	73.65	2.70
200	197.32	4.08	0.05	74.55	0.91
300	295.98	4.16	0.09	76.13	1.57
400	394.64	4.20	0.04	76.84	0.71

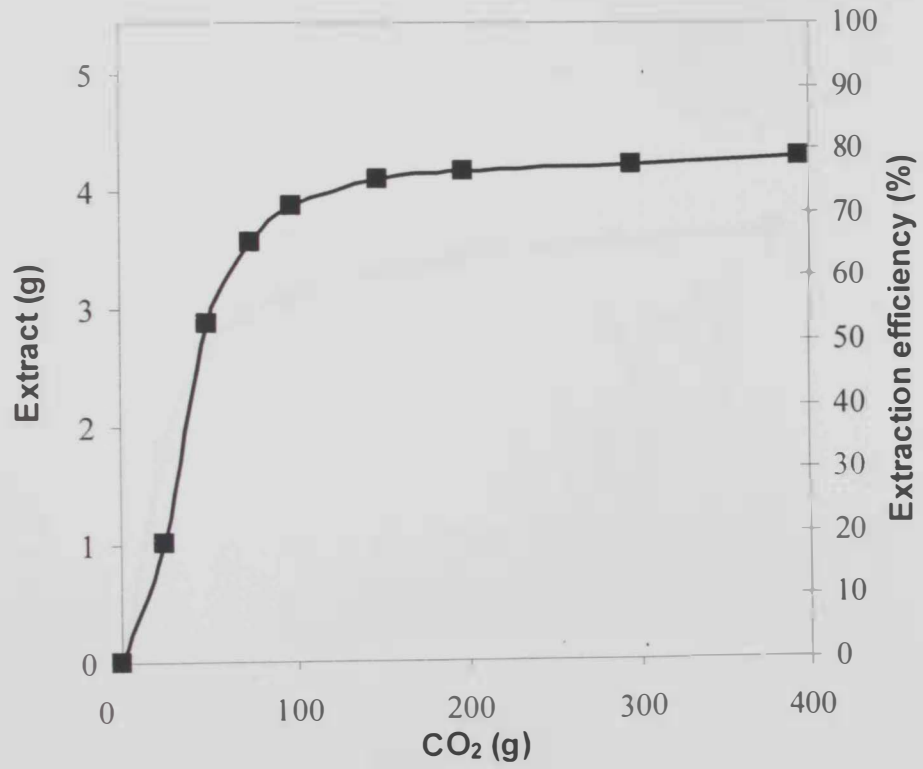


Final Extraction Efficiency % =	76.84

Run Number: 15

Conditions			
Temperature (°C)	Pressure (bar)	Flow Rate (ml/min)	Fluid Type
80	350	1	Pure CO_2
CO_2 Density (g) = 0.98661		Initial oil mass (g) = 5.4531 Sample weight (g) = 60.01	

CO_2 Volume (ml)	CO_2 Mass (g)	Extract weight (g)		Efficiency (%)	
		cumulative	absolute	cumulative	absolute
0	0.00	0.00	0.00	0.00	0.00
25	24.67	1.02	1.02	18.70	18.70
50	49.33	2.88	1.86	52.76	34.06
75	74.00	3.58	0.70	65.66	12.90
100	98.66	3.88	0.29	71.06	5.41
150	147.99	4.11	0.24	75.43	4.36
200	197.32	4.17	0.06	76.51	1.09
300	295.98	4.23	0.06	77.59	1.08
400	394.64	4.29	0.06	78.69	1.10

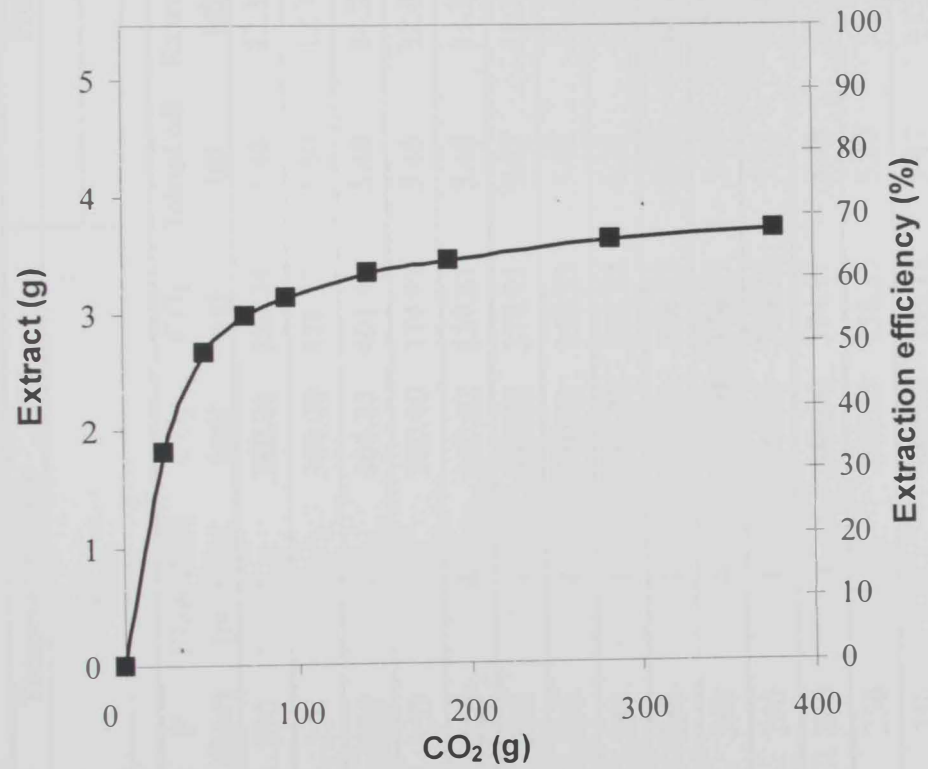


Final Extraction Efficiency % =	78.69

Run Number: 16

Conditions			
Temperature (°C)	Pressure (bar)	Flow Rate (ml/min)	Fluid Type
160	250	1	Pure CO_2
CO_2 Density (g) = 0.94298			Initial oil mass (g) = 5.4656
			Sample weight (g) = 60.11

CO_2 Volume (ml)	CO_2 Mass (g)	Extract weight (g)		Efficiency (%)	
		cumulative	absolute	cumulative	absolute
0	0.00	0.00	0.00	0.00	0.00
25	23.57	1.81	1.81	33.16	33.16
50	47.15	2.67	0.85	48.80	15.64
75	70.72	2.97	0.30	54.34	5.54
100	94.30	3.13	0.16	57.33	2.99
150	141.45	3.33	0.20	60.98	3.65
200	188.60	3.45	0.12	63.09	2.11
300	282.89	3.61	0.16	66.01	2.92
400	377.19	3.70	0.09	67.66	1.65

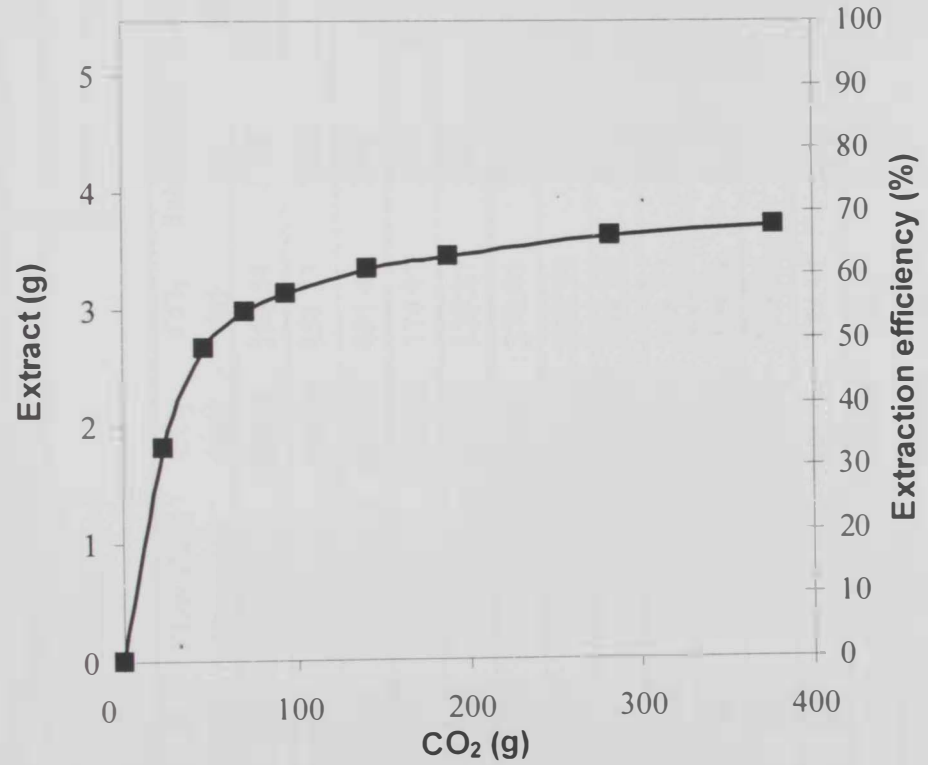


Final Extraction Efficiency % = 67.66

Run Number: 16

Conditions			
Temperature (°C)	Pressure (bar)	Flow Rate (ml/min)	Fluid Type
160	250	1	Pure CO_2
CO_2 Density (g) =	0.94298	Initial oil mass (g) =	5.4656
		Sample weight (g) =	60.11

CO_2 Volume (ml)	CO_2 Mass (g)	Extract weight (g)		Efficiency (%)	
		cumulative	absolute	cumulative	absolute
0	0.00	0.00	0.00	0.00	0.00
25	23.57	1.81	1.81	33.16	33.16
50	47.15	2.67	0.85	48.80	15.64
75	70.72	2.97	0.30	54.34	5.54
100	94.30	3.13	0.16	57.33	2.99
150	141.45	3.33	0.20	60.98	3.65
200	188.60	3.45	0.12	63.09	2.11
300	282.89	3.61	0.16	66.01	2.92
400	377.19	3.70	0.09	67.66	1.65



Final Extraction Efficiency % =	67.66

SFE experimental results for modified CO_2 with 5% (v/v) heptane

Temperature (°C)	Pressure (bar)	Density of CO_2
25	250	0.94298
	350	0.98661

Run No.	T (°C)	P (bar)	Flow Rate (ml/min)	CO_2 (ml)	CO_2 (g)	Initial oil (g)	Extract (g)	Heptane in the extract (g)	Extracted hydrocarbons (g)	Extraction efficiency (%)
17	160	250	4	380.01	358.34	5.48	12.11	8.085	4.029	73.570
18	80	250	4	380.00	358.33	5.50	12.34	8.130	4.206	76.515
19	160	350	1	406.85	401.40	5.48	14.23	9.533	4.693	85.617
20	80	350	1	380.00	374.91	5.45	12.06	6.741	5.322	97.657
21	80	250	4	360.42	339.87	5.46	11.79	7.290	4.502	82.504
22	160	350	1	380.00	374.91	5.47	13.20	8.575	4.623	84.525
23	160	250	4	380.00	358.33	5.47	12.51	7.973	4.534	82.885
24	80	250	1	380.00	358.33	6.25	11.94	6.724	5.213	83.359
25	160	250	1	380.00	358.33	5.47	12.55	8.675	3.873	70.846
26	160	350	4	380.00	374.91	5.47	12.72	7.910	4.810	87.932
27	80	250	1	380.00	358.33	5.53	12.48	8.195	4.282	77.432
28	80	350	4	380.00	374.91	5.48	12.37	7.630	4.742	86.481
29	160	250	1	380.00	358.33	5.50	12.34	8.210	4.133	75.207
30	80	350	1	360.00	355.18	5.47	11.84	7.090	4.751	86.860
31	80	350	4	380.53	375.43	5.48	12.89	8.015	4.871	88.882
32	160	350	4	380.40	375.31	5.46	13.14	8.880	4.257	77.892

SFE experimental results for modified CO_2 with 5% (v/v) toluene

Temperature (°C)	Pressure (bar)	Density of CO_2
25	250	0.94298
	350	0.98661

Run No.	T (°C)	P (bar)	Flow Rate (ml/min)	CO_2 (ml)	CO_2 (g)	Initial oil (g)	Extract (g)	Toluene in the extract (g)	Extracted hydrocarbons (g)	Extraction efficiency (%)
33	80	250	1	380.00	358.33	5.47	13.66	9.640	4.016	73.473
34	160	250	4	336.49	317.30	5.46	17.18	13.555	3.623	66.390
35	80	350	4	380.00	374.91	5.46	16.59	12.135	4.454	81.571
36	80	250	4	380.00	358.33	5.47	17.04	13.050	3.994	73.075
37	160	250	1	380.00	358.33	5.47	17.55	13.425	4.122	75.371
38	80	350	4	380.01	358.34	5.46	15.98	11.585	4.393	80.445
39	80	250	4	382.04	360.26	5.46	17.35	13.520	3.833	70.222
40	160	350	1	380.00	358.33	5.46	16.88	13.030	3.852	70.530
41	80	350	1	380.00	358.33	5.46	18.73	14.670	4.058	74.336
42	80	250	1	380.00	358.33	5.47	17.44	13.140	4.298	78.623
43	160	350	4	380.00	358.33	5.46	16.92	13.225	3.700	67.747
44	160	250	1	380.00	358.33	5.47	17.97	14.180	3.794	69.326
45	160	350	4	380.00	358.33	5.46	16.68	12.720	3.962	72.516
46	160	250	4	380.00	358.33	5.46	17.70	13.856	3.843	70.377
47	160	350	1	380.00	358.33	5.47	18.05	14.210	3.838	70.223
48	80	350	1	380.00	358.33	5.47	17.20	12.780	4.424	80.930

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ملخص الأطروحة

إنّ تقنية الاستخلاص باستخدام مواد عند الظروف ما فوق الحرجة للمادة و التي تعرف بـ (Supercritical Fluids) هي من التقنيات الحديثة و الفعالة في عمليات فصل المواد و استخلاصها، و التي لها العديد من التطبيقات العملية الهامة في المجال البيني و الصناعة البترولية. فعملية الاستخلاص أو الفصل باستخدام غاز ثاني أكسيد الكربون في الظروف ما فوق الحرجة للمادة يمكن تطبيقها كتقنية فعالة لمعالجة و تنظيف التربة الملوثة بالبقع النفطية. و على صعيد آخر، فإن عملية الاستخلاص باستخدام غاز ثاني أكسيد الكربون في الظروف ما فوق الحرجة للمادة يمكن تطبيقها كتقنية لتحفيز إنتاجية آبار النفط ، لذلك فإن استخدام غاز ثاني أكسيد الكربون تحت الظروف فوق الحرجة للمادة في عمليات الاستخلاص و الفصل يساهم في تحقيق فوائد بيئية و اقتصادية على حد سواء.

في هذه الدراسة تمّ استخدام غاز (ثاني أكسيد الكربون) في الظروف ما فوق الحرجة للمادة، لاستخلاص المركبات (الهيدروكربونية) من تربة مشبّعة بالنفط الخام من حقل "بو حصا" الإماراتي. و تمّ دراسة تأثير كل من معدلي تدفق غاز ثاني أكسيد الكربون (1 و 4 مل/ثانية)، و تأثير درجتي الحرارة (80 و 160 درجة مئوية) و تأثير ضغطي الغاز (250 و 350 بار) على كفاءة غاز (ثاني أكسيد الكربون) في عملية الاستخلاص. بالإضافة لدراسة تأثير إضافة كل من المذيب العضوي (الهبتان/ أو / التولوين) بمعدل (5 %) من حجم السائل المستخدم في عملية الاستخلاص .

لقد أظهرت هذه الدراسة بأن أفضل الظروف لاستخلاص المركبات الهيدروكربونية بما يعادل (92%) كانت عند استخدام درجة الحرارة (80 مئوية) و تحت ضغط قدره (350 بار)، باستخدام غاز (ثاني أكسيد الكربون) المعدل بالمذيب العضوي (الهبتان) بنسبة (5%) من حجم السائل المستخدم. و من خلال تحليل و دراسة المواد المتبقية في التربة بعد عملية الاستخلاص بغاز غاز (ثاني أكسيد الكربون) أظهرت النتائج بأنّ هذه التقنية فعالة في معالجة التربة الإماراتية الملوثة بالمواد النفطية من حقل (بوحصا). حيث استطاعت هذه التقنية إزالة (93 %) من المواد الهيدروكربونية البترولية الكلية (TPH) من التربة الملوثة. بالإضافة لذلك لقد أظهرت الدراسة انخفاضاً واضحاً في مستويات المركبات الهيدروكربونية الحلقية (PAHs) الموجودة في التربة الملوثة. كما تمّ في هذا العمل دراسة عملية استخلاص المركبات الهيدروكربونية من صخور (اللايمستون) المشبعة جزئيا بالنفط الخام عند ظروف مشابهة للظروف الحقل النفطي (120 درجة مئوية و 300 بار).

جامعة الإمارات العربية المتحدة
عمادة الدراسات العليا
برنامج ماجستير علوم البيئة

استخلاص المركبات الهيدروكربونية و تقليل الرواسب العضوية من النفط الخام

باستخدام غاز ثاني أكسيد الكربون

رسالة مقدمة من /

عادل أديب عزام

إلى
عمادة الدراسات العليا
جامعة الإمارات العربية المتحدة
استكمالا لمتطلبات الحصول على
درجة الماجستير في علوم البيئة

المشرفون

المشرف الأساسي	المشرف المساعد
الدكتور : علي حسن المرزوقي	البروفيسور : عبد الرزاق يوسف زكري
الدكتور المساعد في الهندسة الكيميائية	بروفيسور في الهندسة البترولية
قسم الهندسة الكيميائية و البترولية	قسم الهندسة الكيميائية و البترولية
كلية الهندسة	كلية الهندسة
جامعة الإمارات العربية المتحدة	جامعة الإمارات العربية المتحدة

يناير 2009

جامعة الإمارات العربية المتحدة
عمادة الدراسات العليا
برنامج ماجستير علوم البيئة

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استكمالا لمتطلبات الحصول على
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يناير ٢٠٠٩

جامعة الإمارات العربية المتحدة
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